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THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

X. REACTIONS WITH α-METHYLCINNAMIC ACID.

BY E. P. KOHLER.

The principal object in investigating the reaction with methylcinnamic acid was to determine the influence of a "positive" group in the α-position of unsaturated esters. In an account[1] of the results obtained with benzalpropiophenone it was shown that the reactions with this substance, which has α-methyl, are exactly like those with benzalacetophenone. Since the publication of that account, Blaise and Courtot[2] have studied the reaction between Grignard's reagent and methacrylic acid and obtained results that they attribute to direct union of the reagent to the double linkage between carbon atoms. With methylmagnesium iodide, for example, they got, in addition to the tertiary alcohol expected, variable quantities of a saturated ketone, formed according to the equation :

[1] THIS JOURNAL, 31, 655.
[2] Compt. rend., 140, 370.

$CH_3 : C(CH_3)COOC_2H_5 + 2CH_3MgI + 2H_2O =$
$C_2H_5CH(CH_3)COCH_3 + 2Mg(OH)I + C_2H_5OH.$

This result they interpret as follows:

$CH_3 : C(CH_3)COOC_2H_5 \rightarrow$
$CH_3CH_2C(CH_3)(MgI)C(CH_3)(OC_2H_5)OMgI \rightarrow$
$CH_3CH_2CH(CH_3)COCH_3.$

The authors offer no evidence in support of this interpretation and it seemed much more likely that the result was due to 1,4-addition, *viz.*:

I. $CH_3 : C(CH_3)COOC_2H_5 + CH_3MgI =$
$CH_3 : C(CH_3)COCH_3 + MgIOC_2H_5;$

II. $CH_3 : C(CH_3)COCH_3 + CH_3MgI =$
$CH_3CH_2C(CH_3) : C(OMgI)CH_3;$

III. $CH_3CH_2C(CH_3) : C(OMgI)CH_3 + H_2O =$
$C_2H_5C(CH_3) : C(OH)CH_3 \rightarrow C_2H_5CH(CH_3)COCH_3.$

This view is established by the results described in the present paper.

The first reaction between methyl α-methylcinnamate and an organic magnesium derivative invariably consists in the replacement of methoxyl by a hydrocarbon residue, the product being an unsaturated ketone. As was shown in an earlier paper, this replacement reaction is greatly influenced by the nature of the group in the α-position. The effect of α-methyl is shown by the following table:

Ester.	Magnesium compound.	Per cent of product formed by replacement of OR.	Per cent of product formed by 1,4-addition.
$C_6H_5CH : C(CH_3)COOR$	C_6H_5MgBr	96	4
"	CH_3MgI	100	0
$C_6H_5CH : CHCOOR$	C_6H_5MgBr	50	50
"	CH_3MgI	100	0
$C_6H_5CH : CBrCOOR$	C_6H_5MgBr	30	70
"	CH_3MgI	100	0
$C_6H_5CH : C(C_6H_5)COOR$	C_6H_5MgBr	0	100
"	CH_3MgI	100	trace
$C_6H_5CH : C(CN)COOR$	C_6H_5MgBr	0	100
"	CH_3MgI	0	100

In case an excess of reagent is present the unsaturated ketone immediately reacts with a second molecule and forms either the magnesium derivative of a tertiary alcohol by addition to carbonyl, or the derivative of an unsaturated alcohol by 1,4-addition, as represented by equation II. The most convincing proof of 1,4-addition was obtained when the magnesium derivative was carefully decomposed with iced acid. The resulting ethereal solution, when heated, gave only unsaturated ketone; but when it was evaporated at low temperatures, in a current of moist air or oxygen, the result was a peroxide. This behavior, as was shown in my last paper, is typical of the unsaturated alcohols obtained by 1,4-addition to ketones:

$$(C_6H_5)_2CHC(CH_3) : C(OH)C_6H_5 + O_2 = (C_6H_5)_2CHC(CH_3)\underset{\displaystyle O}{\overset{\displaystyle O}{\diagup\!\diagdown}}C(OH)C_6H_5.$$

In this connection a number of experiments were performed for the purpose of determining to what extent this peroxide formation can be relied upon to prove 1,4-addition. All the solutions that were tried were obtained by decomposing magnesium compounds that were known to be 1,4-addition products of unsaturated esters or ketones. The results are shown in the following table:

Substance.	Amount of peroxide.
$(C_6H_5)_2CHCH : C(OH)C_6H_5$	none
$C_6H_5CH(CH_3)CH : C(OH)C_6H_5$	"
$(C_6H_5)_2CHC(CH_3) : C(OH)C_6H_5$	95 per cent
$C_6H_5CH(CH_3)C(CH_3) : C(OH)C_6H_5$	92 "
$(C_6H_5)_2CHCBr : C(OH)C_6H_5$	none
$(C_6H_5)_2CHC(C_6H_5) : C(OH)C_6H_5$	96 per cent
$C_6H_5CH(C_2H_5)C(C_6H_5) : C(OH)C_6H_5$	"
$(C_6H_5)_2CHCH : C(OH)OC_2H_5$	none
$(C_6H_5)_2CHC(C_6H_5) : C(OH)OCH_3$	"
$C_6H_5CH(C_2H_5)C(C_6H_5) : C(OH)OCH_3$	"
$(C_6H_5)_2CHC(C_2H_5) : C : NH$	"

As will be seen, peroxides were obtained from enols derived from ketones with a hydrocarbon residue in the α-position and only from these. In all other cases the rearrangement from

the enolic to the corresponding saturated compound took place so rapidly that the latter began to separate from solution even before all of the magnesium derivative had been decomposed. These results may, at first sight, appear to be at variance with a very general conclusion reached by a careful study of tautomerism, namely, that alkyl derivatives are less extensively enolized than the substances from which they are derived. That conclusion, however, refers only to a final condition, while these results depend upon the rate at which an enol, that is obtained by indirect methods, passes into the only stable form.

EXPERIMENTAL PART.

The methylcinnamic acid used in the following experiments was made by Perkin's reaction, using benzaldehyde, propionic anhydride and sodium propionate. By neutralizing the product with an excess of sodium carbonate and crystallizing the salts from a solution of the carbonate it was possible to separate 2 sodium salts, corresponding to the 2 acids described by Raikow[1] and by Dain.[2] From a solution of the less soluble salt that separates from the sodium carbonate solution in solid form, acids precipitated pure, high-melting acid. This crystallized from ligroin in needles, melting at 81°. The more soluble salt that accumulated in the filtrates gave, mainly, the low-melting acid, which separated from ligroin in plates and melted at 74°. In this way it was comparatively easy to get the isomeric acids in any desired quantity, but all efforts to get the corresponding methyl esters failed. All methods of procedure gave the same ester from both acids.

Reactions with Phenylmagnesium Bromide.

In a preliminary experiment the reagent was very slowly siphoned into a dilute ethereal solution that contained a little more than one equivalent of ester and was cooled in a freezing mixture. The oil obtained by treating the resulting magnesium derivative in the usual way, was fractioned under diminished pressure and thus separated into unchanged ester

[1] Ber. d. chem. Ges., **20**, 3397.
[2] Centrabl., 1898, I., p. 674.

melting at 39°, a pale yellow oil boiling at 212° (25 mm.) and a small quantity of solid melting at 102°. The oil forming the principal product of the reaction was identified as benzalpropiophenone. It reduced a solution of potassium permanganate in acetone and gave a phenylhydrazone melting at 131°. The solid melting at 102° was diphenylpropiophenone, previously described[1] as the sole product of the reaction between benzalpropiophenone and phenylmagnesium bromide. This experiment shows that the first reaction between methyl methylcinnamate and phenylmagnesium bromide consists in the replacement of methoxyl by phenyl.

When the reaction is carried out in the ordinary manner—the ester being added to a cooled, ethereal solution of the magnesium compound—the unsaturated ketone first formed immediately combines with a second molecule of phenylmagnesium bromide and the sole product is diphenylbutyrophenone. By operating in boiling ethereal solution it is possible to get a small quantity of saturated ester (ca 3 per cent) formed by direct addition to the ester. This fact was established by boiling the entire product with alcoholic potassium hydroxide and extracting the salt with water. From the aqueous solution hydrochloric acid precipitated a solid which was identified by comparison with a specimen of diphenylisobutyric acid on hand.

Triphenylmethylpropenyl Benzoate, $(C_6H_5)_3CHC(CH_3) : C(C_6H_5)OCOC_6H_5$.—To prove that diphenylbutyrophenone is formed by 1,4-addition, the intermediate magnesium derivative was treated with slightly more than 1 equivalent of benzoyl chloride. The product, purified by recrystallization from a mixture of chloroform and alcohol, melted at 122°. Analysis:

0.1155 gram substance gave 0.3670 gram CO_2 and 0.0623 gram H_2O.

	Calculated for $C_{39}H_{32}O_2$.	Found.
C	86.1	86.5
H	5.9	5.9

[1] THIS JOURNAL, 31, 655.

The substance crystallizes in needles. It is readily soluble in acetone and chloroform, moderately in boiling alcohol and ether, very slightly in ligroin. Cold alcoholic potassium hydroxide rapidly hydrolyzes it to benzoic acid and diphenylbutyrophenone.

Diphenylbrombutyrophenone, $(C_6H_5)_2CHCBr(CH_3)COC_6H_5$.—The magnesium derivative of triphenylmethylpropenol readily reacts with 1 atom of bromine. The product separates from a mixture of ether and ligroin in large, lustrous tables, melting at 93°. The same substance is obtained when a chloroform solution, containing calculated quantities of diphenylbutyrophenone and bromine, is warmed on a water-bath, but the yield obtained by this method is much poorer and it is difficult to get rid of secondary products. Analysis:

0.1372 gram substance gave 0.3500 gram CO_2 and 0.0630 gram H_2O.

	Calculated for $C_{29}H_{19}OBr$.	Found.
C	69.65	69.50
H	5.01	5.12

The bromide is readily soluble in chloroform, moderately in alcohol and ether, sparingly in ligroin. It has not, as yet, been possible to eliminate hydrobromic acid and get an unsaturated ketone. Concentrated, alcoholic potassium hydroxide, which readily removes hydrobromic acid from analogous substances that have hydrogen[1] or phenyl[2] in place of methyl, in this case produces deep-seated decomposition, resulting in a number of products of which benzoic acid and diphenylmethane have been isolated and identified.

Triphenylmethylpropenol Peroxide,

$$(C_6H_5)_2CHC(CH_3)\underset{\displaystyle O}{\overset{\displaystyle O}{\diagup\!\diagdown}}C(OH)C_6H_5$$

.—When the magnesium derivative obtained by treating either benzalpropiophenone or methyl methylcinnamate is very carefully decomposed with iced hydrochloric acid, and the resulting ethereal solution

[1] THIS JOURNAL, 33, 41.
[2] *Ibid.*, 36, 195.

rapidly evaporated in a current of air or oxygen, as directed in a previous paper, about 96 per cent of the product is obtained in the form of a peroxide. In solution this is much less stable than the peroxides previously described, hence it is difficult to get a perfectly pure substance. The crude product was first dried thoroughly over phosphorus pentoxide in a vacuum desiccator, then repeatedly extracted with small quantities of low-boiling ligroin and finally recrystallized from a mixture of absolute ether and low-boiling ligroin. It separated in colorless needles, melting at 127°, and was readily soluble in all common organic solvents except ligroin. Analysis:

I. 0.1883 gram substance gave 0.5470 gram CO_2 and 0.1020 gram H_2O.

II. 0.1554 gram substance gave 0.4535 gram CO_2 and 0.0828 gram H_2O.

	Calculated for $C_{22}H_{20}O_2$.	Found. I.	Found. II.
C	79.5	79.22	6.02
H	6.0	79.52	5.94

The Molecular Weight in Boiling Ether

K = 21.6.

Solvent. Grams.	Substance. Grams.	Rise in boiling point.	Molecular weight.
45.42	0.8360	0.127	313
"	1.4150	0.209	322
"	2.0540	0.302	323
	Calculated for $C_{22}H_{20}O_2$,		332

When perfectly pure the peroxide seems to be stable at the ordinary temperature. A specimen that has been kept in an open vessel for a year has changed neither in color nor melting point. Impure specimens rapidly turn yellow and occasionally explode. On a steam-bath the pure substance gradually softens, then explodes with a flash but without detonation. The same explosion takes place the instant the substance is melted. The products of decomposition by heat are quite different from those obtained from the peroxide that differs from this only in having phenyl in place of methyl.

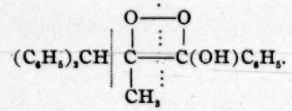
By exploding 25 grams in small portions and treating the resulting products as described in the last paper,[1] it was possible to isolate 7.2 grams of benzoic acid, 9.1 grams of a solid melting at 208°–210°, and a small quantity of diphenylmethane. The solid was purified by recrystallization from chloroform, from which it separated in flat needles. Analysis:

0.1540 gram substance gave 0.5280 gram CO_2 and 0.0910 gram H_2O.

	Calculated for $C_{26}H_{22}$.	Found.
C	93.4	93.5
H	6.6	6.5

Composition and melting point indicated symmetrical tetraphenylethane. It was identified as such by comparison with a specimen made from diphenylbrommethane.

The remaining products of decomposition were not identified, but it is evident that the peroxide molecule breaks down at two points:



Decomposition at these points should give 8.4 grams of benzoic acid and 12.5 grams of tetraphenylethane.

A similar decomposition into benzoic acid and tetraphenylethane took place when the peroxide was warmed with concentrated alcoholic potassium hydroxide; but by adding it slowly to a dilute solution, that was kept cool with ice-water, it was possible to isolate an intermediate product. This separated slowly from the alkaline solution in colorless plates. It was purified by recrystallization from a mixture of acetone and alcohol. It is readily soluble in chloroform, moderately in acetone, very slightly in alcohol and ether. The melting point is 188°. Analysis:

[1] THIS JOURNAL, 36, 189.

I. 0.1378 gram substance gave 0.4205 gram CO_2 and 0.0713 gram H_2O.

II. 0.1700 gram substance gave 0.5210 gram CO_2 and 0.0963 gram H_2O.

	Calculated for $C_{22}H_{20}O_2$.	Found. I.	Found. II.
C	83.6	83.22	83.7
H	6.3	6.5	6.3

Molecular Weight in Boiling Ether.

K = 26.1.

Solvent. Grams.	Substance. Grams.	Elevation of boiling point.	Molecular weight.
20.10	0.4890	0.213	298
"	0.7830	0.361	282
"	0.9810	0.436	293
	Calculated for $C_{22}H_{20}O_2$,		316

The substance is evidently a reduction product formed from the peroxide by loss of one atom of oxygen. On distillation it decomposes into tetraphenylethane, benzoic acid and volatile hydrocarbons. Reagents like potassium hydroxide, hydroxylamine, acetic anhydride and glacial acetic acid produce essentially the same decomposition, but the principal product is diphenylmethane, in place of tetraphenylethane. The first definite clue as to the structure was supplied by the behavior towards methylmagnesium iodide. When a solution of this reagent was siphoned into an excess of the substance methane was evolved, until the solution contained approximately 1 molecule of the reagent for 1 of the substance. This proved the presence of one, and only one, hydroxyl group, and suggested as the most probable formula :

$$(C_6H_5)_2CHC(CH_3)(OH)COC_6H_5.$$

This structure was definitely established by the following method of preparation :

α-Bromdiphenylbutyrophenone, as stated above, is completely decomposed by concentrated, alcoholic potassium hydroxide, but by cautiously adding dilute, aqueous hydroxide, in small quantities, to a cooled solution of the bromide, it is

possible to replace the bromine quantitatively with hydroxyl. The product of this reaction is identical with that obtained from the peroxide. That substance is, therefore, α-hydroxydiphenylbutyrophenone. The only other substance of this composition that could be obtained from the bromide would be the corresponding β-hydroxy derivative, which might be formed by elimination of hydrobromic acid and subsequent addition of water. The substance cannot be a β-hydroxy compound, however, because it gives tetraphenylethane on distillation and diphenylmethane with potassium hydroxide.

Reaction with Methylmagnesium Iodide.

Methyl methylcinnamate reacts with 2 molecules of methylmagnesium iodide, even though the magnesium compound be slowly siphoned into an excess of ester. The first reaction doubtless results in the formation of an unsaturated ketone, but this combines with more reagent so readily that it is impossible to separate the replacement and addition reactions. As is the case with benzalacetone and other methyl ketones, so here the addition is wholly to the carbonyl group. The product is an oil that, when heated under diminished pressure, begins to lose water at 150° and passes into a hydrocarbon that boils at 165° (30 mm.). Analysis:

0.2073 gram substance gave 0.6917 gram CO_2 and 0.1645 gram H_2O.

	Calculated for $C_{11}H_{14}$.	Found.
C	91.1	91.0
H	8.9	9.2

The substance is phenyldimethylbutadiene, formed according to the equation:

$$C_6H_5CH : C(CH_3)C(CH_3)_2OH = H_2O + C_6H_5CH : C(CH_3)C(CH_3) : CH_2.$$

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
June, 1906.

Contributions from the Chemical Laboratory of Harvard College.

ON ETHYL PYROMUCYLACETATE.

[PRELIMINARY PAPER.]

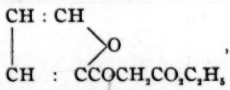
By Henry A. Torrey and J. E. Zanetti.

This compound was first prepared by Sandelin[1] in 1900, by the action of sodium on a mixture of 2 molecules of ethyl acetate and 1 of ethyl pyromucate. The aim of his research was, however, the preparation of methylfurfuryl ketone, which he obtained by saponifying the ester with concentrated sulphuric acid, the ester itself being but little investigated. Subsequently, Bouvealt,[2] in his research on acetyl furfurane, repeated Sandelin's work on the ester but proceeded no further. Since the work which has been done upon this substance is so inconsiderable, we have undertaken its investigation in continuation of the work in this laboratory of the late Professor H. B. Hill on the furfurane derivatives.

The ester itself was obtained by Sandelin's method as a light yellow, heavy oil, boiling at 143°–145° (10 mm.). By using small amounts at a time, 15 grams of ethyl pyromucate and 20 grams of ethyl acetate, the best yields of 40–50 per cent were obtained. The use of potassium instead of sodium had no perceptible advantage. Both the ethyl acetate and the ethyl pyromucate were purified and freed from water before using, the ethyl acetate by drying over calcium chloride and distilling and the ethyl pyromucate by distilling under reduced pressure. This was found to be necessary, as some pyromucic acid is always carried down by the ethyl pyromucate in its preparation and distils over with the pyromucylacetic ester if not removed beforehand. The product of the first distillation carries over with it a sharp smelling compound which, if allowed to remain with the ester, slowly turns it dark. If the ester is redistilled, however, and the first fraction rejected, it keeps its light color for weeks and has practically no smell. Only after long standing does it become brown.

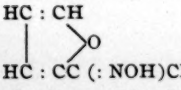
[1] Ber. d. chem. Ges., **33**, 492.
[2] Bull. Soc. Chim., [3], **25**, 435.

If ethyl pyromucylacetate is given the ketone formula, it would be represented thus :



but doubtless tautomeric relationships will be found here as with ethyl acetacetate and similar compounds. As would be expected, ethyl pyromucylacetate shows the characteristic ketone reactions, forming an oxime, a semicarbazone and, with phenylhydrazine, a pyrazolone.

Oxime of Ethyl Pyromucylacetate,



.—This body was obtained by allowing 1 molecule of hydroxylamine hydrochloride, treated with a solution of sodium acetate, to act on 1 molecule of the ester, in a dilute alcohol solution. After letting the mixture stand for about 3 hours at room temperature and adding considerable water, the mass of long, white crystals was filtered by suction and recrystallized from dilute alcohol. After 3 crystallizations the constant melting point, 131°–132°, was reached. Thus crystallized, the oxime consists of long, silky needles, soluble in a mixture of ether and alcohol. Analysis of the substance dried *in vacuo* over sulphuric acid :

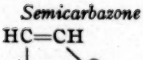
I. 0.3995 gram substance gave 28.80 cc. of nitrogen at 20°.6 and 753 mm.

II. 0.1887 gram substance gave 12.68 cc. of nitrogen at 15°.2 and 760 mm.

III. 0.4008 gram substance gave 26.70 cc. nitrogen at 23° and 747 mm.

	Calculated for $C_9H_{11}O_4N$.	Found. I.	II.	III.
N	7.11	8.15	7.86	7.34

Semicarbazone of Ethyl Pyromucylacetate,



.—This compound was formed by treating 1 molecule of the ester, in dilute alcohol solution, with 1 molecule of semicarbazide hydrochloride and the corresponding amount of sodium acetate. After standing for about 3 hours white crystals separated out. These were filtered off, washed with water and recrystallized from hot, absolute alcohol until a constant melting point was reached at 142°–144°. The substance crystallizes in small, flat, rhombic plates which decompose slightly on melting. They are soluble in hot, absolute alcohol, hot benzene and hot chloroform, but insoluble in ligroin, hot or cold.

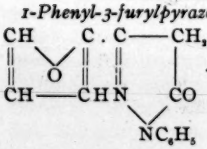
Analysis of substance dried over concentrated sulphuric acid *in vacuo* :

I. 0.1953 gram substance gave 30.95 cc. nitrogen at 25°.7 and 757 mm.

II. 0.2502 gram substance gave 41.38 cc. nitrogen at 22°.5 and 747 mm.

	Calculated for $C_{10}H_{12}O_4N_2$.	Found. I.	Found. II.
N	17.57	17.55	18.37

1-Phenyl-3-furylpyrazolone,



.—This compound was prepared by Sandelin, by the action of 1 molecule of phenylhydrazine on 1 molecule of the ester, at 100°. After about 0.5 hour the mass solidifies and, by washing with alcohol and crystallizing from hot alcohol, the body is obtained as a white, crystalline mass of minute leaflets, melting at 179°. This substance has proved to be a very interesting one and we have prepared several of its derivatives. It is readily soluble in alkalies, pre-

cipitating from the solution on neutralizing with acid. If excess of acid be added, however, it redissolves. The pyrazolone itself, untreated with alkali, is soluble with difficulty only in concentrated acid. The above formula is that given by Sandelin. It is possible, however, that it may have a tautomeric form.

Acetyl Phenylfurylpyrazolone, $C_{13}H_9O_2N_2.COCH_3$. — This compound was readily obtained by dissolving the pyrazolone in boiling acetic anhydride and pouring the solution into water, when an oil separated which, on scratching, crystallized to a yellowish-white mass. The crystals were filtered off and recrystallized from ligroin several times to a constant melting-point. The melting point is not very sharp, lying between 69°–72°. Under the microscope the crystals appeared as flat, transparent prisms, slightly yellow in color. They are soluble in alcohol, benzene and ether without difficulty, but insoluble in cold ligroin.

0.4196 gram substance gave 39.81 cc. nitrogen at 25° and 756 mm.

	Calculated for $C_{15}H_{12}O_3N_2$.	Found.
N	10.44	10.52

The *benzoyl derivative*, $C_{13}H_9O_2N_2.COC_6H_5$, was obtained by the Schotten-Baumann reaction. The pyrazolone was dissolved in sodium hydroxide and an excess of benzoyl chloride added. After some time a yellowish mass of crystals separated. These were filtered, washed and crystallized from dilute alcohol, whence they were obtained as white needles which, after 3 crystallizations, gave the constant melting point 113°–114°. The body is soluble in alcohol and ether.

0.2084 gram substance, dried over concentrated sulphuric acid, gave 15.81 cc. nitrogen at 21° and 763 mm.

	Calculated for $C_{20}H_{14}O_3N_2$.	Found.
N	8.48	8.69

The *nitroso derivative*, $C_{13}H_9N_2O_2.NO$, was obtained by adding to an acid solution of the pyrazolone, in dilute alcohol, di-

lute sodium nitrite until starch-iodide paper indicated the presence of an excess of nitrous acid. The nitroso body separates out as a bright red precipitate as the sodium nitrite is added. It dissolves in dilute alcohol on warming, and, on cooling, separates out as an amorphous precipitate. No trace of crystallization could be detected under the microscope, even from solutions allowed to evaporate spontaneously. The body is soluble in alcohol, benzene, methyl alcohol, ether, chloroform and acetone, but insoluble in water. It gives no sharp melting point, but begins to soften at about 170° and gradually melts till at 183°–184° it decomposes, giving off bubbles of gas and becoming dark brown. It is very hygroscopic, gaining as much as 4 milligrams in the course of a weighing if this be carried on without protection from the air. Dried over sulphuric acid *in vacuo*:

0.1961 gram substance gave 27.30 cc. nitrogen at 21° and 772 mm.

	Calculated for $C_{12}H_9O_3N_3$.	Found.
N	16.48	16.12

The study of these compounds will be continued in this laboratory.

METATOLYL ETHER AND DERIVATIVES.

By Alfred N. Cook.

Metatolyl ether, $(C_6H_4.CH_3)_2O$, was first obtained by J. H. Gladstone[1] and Alfred Tribe. They prepared aluminum thymolate, which they believed to decompose on heating, into aluminum metacresolate and propylene, the first compound then decomposing into metatolyl ether and other compounds. They made an analysis of the ether and determined its approximate boiling point, but did not investigate its properties further, hence a continuation of the study of the compound was deemed profitable.

Preparation.—All of the phenyl ethers so far obtained have been prepared by distilling the aluminum salts of the corre-

[1] J. Chem. Soc., 41, 11.

sponding phenols, but phenyl ether has also been prepared by several other methods. The preparation of aluminum metacresolate was found to be possible, although this seems to be the only "aluminum phenolate" not obtained by Gladstone and Tribe, perhaps because the action of aluminum on metacresol is brought about in a somewhat different manner from its action on other phenols. It is also possible that the aluminum they employed was much purer than the modern commercial article which was used in this research. From experiments already described[1] it would seem that the action of aluminum on phenols is electrolytic in character, and for the reason that a very pure aluminum would not contain sufficient impurities to set up local action it would be without action upon phenols, unless a catalytic agent like iodine should be employed.

The remarks made in connection with the preparation of aluminum phenolate[2] mostly apply to the preparation of this compound. Gladstone and Tribe found that a little iodine served to start the action of aluminum on several alcohols, phenol, ortho- and paracresol, etc., but the use of iodine or any other catalytic agent, unless aluminum matacresolate be so considered, was found to be of no avail in inducing the action of aluminum on metacresol.

The action was started by simply boiling metacresol with a few grams of aluminum strips, in a flask fitted with a reflux condenser, until the action began. The time required varied within wide limits, but was usually 3 or 4 hours; when once started, however, the action was very energetic and proceeded at a temperature much below the boiling point of metacresol. The action may be started very quickly and at a much lower temperature by simply adding a few grams of powdered aluminum metacresolate and a few strips of aluminum that have already been attacked by the cresol in a previous experiment and therefore have their impurities laid bare, thus supplying the conditions which exist when metacresol has acted on aluminum for a short time. In practice, the flask which had been used in a previous operation was employed, in which there

[1] J. Am. Chem. Soc., 28, 609.
[2] *Ibid.*, 28, 608.

always remained sufficient aluminum metacresolate adhering to the sides of the vessel to start up the action immediately, and very soon even with fresh aluminum slips.

Aluminum metacresolate is a brittle, translucent solid. It varies in color from gray to black and possesses a vitreous luster and a conchoidal fracture. In appearance it is very much like aluminum phenolate. It is usually a little moist with metacresol unless highly heated at the close of its preparation. When distilled *in vacuo* aluminum metacresolate yields a very little metacresol and a very large amount of a substance which boils at 240° (30 mm.) and decomposes when distilled under ordinary atmospheric pressure. It solidifies at room temperature, melts when gently heated and is an entirely different compound from the 2 higher boiling substances obtained by distilling under ordinary atmospheric pressure, which are mentioned below. The odor of the distillate would indicate that a small amount of metatolyl ether was formed, but not sufficient to separate by fractional distillation.

When distilled under ordinary atmospheric pressure, there was obtained a considerable amount of metacresol, a fair yield of metatolyl ether, a solid substance, boiling at about 300° (uncorr.), and a red liquid boiling at approximately 360°. The higher boiling substances were not examined but were set aside for further study when time permits.

From 850 grams of aluminum metacresolate there was obtained, after repeated fractional distillation, 110 grams of purified metatolyl ether and there resulted 150 grams of metacresol. The best yield of the ether was obtained by distilling rapidly. When distilled slowly there was obtained a much larger yield of metacresol and higher boiling substances. It may be noted that the reverse was found to be true in the preparation of phenyl ether from aluminum phenolate, a much larger yield of the ether being obtained when the phenolate was distilled slowly.

Purification.—Gladstone and Tribe extracted the metatolyl ether from the higher boiling substance, which they assumed, provisionally, to be dimethylbenzophenone, by means of

ether and cooling to —20°, at which temperature the substance is only slightly soluble. They seem not to have obtained the red liquid boiling at about 360°. I obtained an equally pure product by repeated simple fractional distillation. After the separation of the metacresol, which boils about 75° lower, had been carried as far as practicable, and discarding each time the fractions boiling above 290°, the liquid was washed with a solution of sodium hydroxide to remove traces of phenol, and dried with calcium chloride by gentle warming on the water-bath. On again distilling for perhaps a dozen times it had a fairly constant boiling point. A still purer product was obtained by distilling off the metatolyl ether with steam, after washing with sodium hydroxide, but the process is somewhat tedious.

Boiling Point.—The boiling point as given by Gladstone and Tribe is 284°–288°, presumably uncorrected. The determination of the boiling point on 2 different samples, one prepared by extracting with ether and the other by fractional distillation, yielded identical results. The boiling point obtained was 290°.5–291°.5 (cor.). The thermometer was calibrated by means of naphthalene and benzophenone and required but a small correction.

Viscosity.—The viscosity was determined with an apparatus designed for use in testing lubricating oil and was not susceptible to a high degree of accuracy.

Table of Viscosity.

Temperature.	Viscosity.	Difference.
15°.5	1.333	. .
30°	1.194	0.139
40°	1.166	0.028
50°	1.139	0.027

It will be noticed that there is a very marked decrease in viscosity between 15°.5 and 30° and above this temperature the decrease is practically constant for 20°. The most rapid decrease was found to be between 15°.5 and 25°. The viscosity of phenyl ether was found to be 1.095 at 30°. The vis-

cosity of metatolyl ether is, therefore, 9.4 per cent greater at the same temperature, notwithstanding its lower specific gravity.

Properties.—Metatolyl ether is an aromatic, oily substance. It has the odor of geraniums, but is considerably less marked in that respect than phenyl ether. The constant breathing of its vapors has a depressing effect upon the system. It is tasteless, but feels like an oil when taken into the mouth. The specific gravity, determined with a pyknometer, was found to be 1.0323 at 21°, average of 3 determinations which did not vary more than 3 parts in the ten-thousandths place. This is nearly 4 per cent less than liquid phenyl ether at the same temperature, notwithstanding its larger molecule. When prepared by distillation, as described above, it is slightly fluorescent and has a yellowish tint which increases with age, but when purified by distilling with steam it is devoid of fluorescence and is almost colorless. It burns readily with a smoky flame, liberating a large amount of soot. It is insoluble in water, but soluble in most of the common organic solvents and also in a strong solution of sodium metacresolate in water, from which it is precipitated on adding a large amount of water. It is volatile with steam, but considerably less so than phenyl ether.

Action of Reagents.—Attempts to prepare a sulphonic acid derivative with dilute and concentrated sulphuric acid, and fuming sulphuric acid, under varying conditions, were without avail. Phenyl ether yields a disulphonic acid with great ease by simply dissolving in an equal volume of sulphuric acid. Monosulphonic acid derivatives of *p*-nitro-*m*-methylphenyl ether and *o*-nitro-*m*-methylphenyl ether are also formed with great readiness and this failure would seem to indicate that the sulphonic acid group entered the nucleus with the nitro group in the nitromethylphenyl ethers.

Endeavors to oxidize the side chains to carboxyl, with chromic acid in acetic acid solution, were unsuccessful. An aqueous solution of chromic and acetic acid does not attack it when boiled. Chromic acid, in glacial acetic acid, oxidizes it to a fine, white powder which is precipitated on standing when

diluted with a large amount of water. The substance is insoluble in alkalies.

Metatolyl ether is not decomposed by long-continued boiling with a strong solution of sodium hydroxide, nor even when heated in a closed tube to 200°, for several hours. In this respect it is like phenetol, anisol and phenyl ether.

When heated with concentrated, or even fairly dilute nitric acid, it yielded a dinitro compound, but not readily. The tendency is to oxidize completely and many attempts were made before success was finally attained. The best results were obtained with fuming nitric acid. Phenyl ether also yields a dinitro derivative with fuming nitric acid.

When the calculated amount of bromine was added to the substance in solution in carbon bisulphide in the dark, or, *per se*, in direct sunlight, heated to the boiling point, or, at the temperature of the boiling water-bath, at room temperature, or cooled to —20°, there was always formed, with equal facility, a dibrom compound which was identical in every instance.

When double the amount of bromine was added, or even a very large excess, there was produced, with equal readiness, a tetrabrom compound under the same varying circumstances.

Some of the tetrabrom compound was always formed in preparing the dibrom derivative by employing the amount required by calculation and there always remained a small quantity of the ether unacted upon, but only in small amount, and they were readily separated by fractional distillation. Likewise a little of the dibrom compound was obtained by employing the calculated amount of bromine to form the tetrabrom derivative, but the action was more clear cut than is usual in similar cases. It proved impossible to induce the substance to absorb more than 4 atoms of bromine no matter how large an excess was added. No carrier was used in these experiments. Hoffmeister[1] found that phenyl ether, when dissolved in carbon bisulphide, absorbed 2 atoms of bromine to the molecule.

I believe, for the following reasons, that the bromine en-

[1] Ann. Chem. (Liebig), 159, 210.

tered the nucleus in these experiments. The bromine derivatives effectually resisted all attempts to prepare from them compounds analogous to benzyl alcohol and benzaldehyde by all of the common methods. The bromine is very firmly linked in these compounds and all attempts to introduce the hydroxyl group in its place were unsuccessful. This is in accordance with what would be expected if the halogen entered the nucleus. Neither of the two compounds, when purified, gave off vapors which attack the mucous membrane of the eyes, as in case of substances formed by the halogen entering the side chain, but when freshly prepared, and before purification, they did have this property, indicating the possible formation of a small quantity of the side chain compounds. Perhaps the halogen might be induced to enter the side chain by employing a still higher temperature, in direct sunlight, but the experiment was not tried on account of lack of both time and material.

Metatolyl ether is markedly different from toluene and its homologues in its action toward bromine, for in these the halogen enters the side chain in direct sunlight, or at the boiling point of toluene, and it enters the nucleus in the dark, when cold.

Dibrommetatolyl Ether, $(CH_3C_6H_3Br)_2O$. — This compound was best prepared by adding very gradually, with constant shaking, a little more than the theoretical amount of bromine to the metatolyl ether, dissolved in several times its weight of carbon bisulphide. The yield was but little short of quantitative. It was purified by repeated distillation, discarding the highest and lowest boiling fractions each time. A portion was obtained which melted at 48°, but began to soften a few degrees lower. The substance boils at 340°–350° (uncorr.) under ordinary atmospheric pressure, and at about 250° (15 mm.). The dibrom compound is a white, crystalline solid, which turns yellow with age. It tends to crystallize in warty aggregations on cooling from the molten state. It is soluble in carbon bisulphide, alcohol, ether and several other organic solvents; sparingly soluble in absolute methyl alcohol and insoluble in water.

The substance was boiled with water and then with a strong solution of potassium hydroxide, in the hope of introducing the hydroxyl group in place of the halogen, but without result. It was then heated in a closed tube, to 200°, for several hours, with a strong solution of sodium hydroxide, but there was no indication of any reaction. Analysis:

	Calculated for $C_{14}H_{10}OBr_2$.	Found.
Br	44.94	44.55

Tetrabrommetatolyl Ether, $(CH_3C_6H_2Br_2)_2O$.—This compound was found to be best prepared by adding an excess of the amount of bromine required by calculation directly to the metatolyl ether and heating on the water-bath to drive off the surplus. The yield was nearly quantitative. The substance was purified by repeated distillation under diminished pressure. It boils at 260°–270° (35 mm.), but decomposes when distilled under ordinary atmospheric pressure.

It is a light yellow, sticky, viscous substance which crystallizes in warty aggregations on standing for some time. It becomes fluid on gently heating and is soluble in carbon bisulphide but insoluble in alcohol, ether and most other common organic solvents. The compound was boiled with water, a strong solution of potassium hydroxide, and with water and precipitated calcium carbonate, respectively, for several hours without any evidence of chemical action. It was then heated in closed tubes with each of these reagents for 3 or 4 hours, at 200°–300°. The tube containing the potassium hydroxide showed some signs of chemical action, but it was by no means complete. The filtrate yielded a precipitate with silver nitrate and a small quantity of a substance, presumably a hydroxymetatolyl ether, was precipitated by neutralizing with an acid. Analysis:

	Calculated for $C_{14}H_{10}OBr_4$.	Found.
Br	62.26	61.85

Dinitrometatolyl Ether, $(CH_3C_6H_2NO_2)_2O$.—It was found best

to prepare this substance in nearly the same manner as Hoffmeister[1] prepared the dinitro derivative of phenyl ether. By means of a dropping funnel fuming nitric acid was gradually and cautiously added to the substance, kept cool by running water, until the metatolyl ether was entirely dissolved. The solution was then poured into water when the nitro derivative was precipitated as a red, viscous mass. By repeatedly rubbing it up with cold water containing sodium hydroxide it finally solidified. It was then purified by repeated crystallization from alcohol and boiling with bone-black. Dinitrometatolyl ether is a yellow, crystalline substance which melts at 112°–113°. It is insoluble in water, but soluble in alcohol, ether, benzene, etc.; 1.4 parts of the substance are soluble in 1000 parts of 87 per cent alcohol at 20°, but it is much more soluble at higher temperatures. Its composition is shown by the analysis of the amino hydrochloride.

Diaminometatolyl Ether Hydrochloride, $(CH_3C_6H_3NH_2HCl)_2O$. —This compound was easily and quickly prepared by reducing the nitro compound, in alcoholic solution, with tin and hydrochloric acid by gentle warming on the water-bath and precipitating the tin with hydrogen sulphide. On account of its great solubility in water, it was found best to purify it by crystallizing from concentrated hydrochloric acid, in which it is much less soluble. The hydrochloride is quite stable even when moist. With alkalies it yields a free *base* which is insoluble in water, but soluble in alcohol and ether. It also is quite stable, but less so than the hydrochloride. The latter yielded 23.98 per cent of chlorine; calculated for $C_{14}H_{18}ON_2Cl_2$ is 23.59 per cent.

A similar study is now being made of paratolyl ether. It will also be extended to the ortho compound as soon as possible.

UNIVERSITY OF SOUTH DAKOTA,
VERMILLION, S. D.,
June 19, 1906.

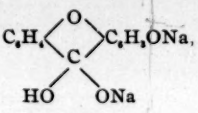
[1] Ann. Chem. (Liebig), 159, 208.

THE ISOMERISM OF ETHYLCOUMARIC AND ETHYLCOUMARINIC ACIDS.

By Arthur Michael and Arthur B. Lamb.

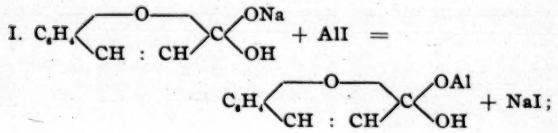
In the course of his synthetical investigations of the substituted cinnamic acids, W. H. Perkin[1] made the interesting observation that methoxycinnamic acid, prepared from *o*-methoxybenzoic aldehyde and acetic anhydride, is not identical with the isomeric substance obtained by the action of methyl iodide on R. Williamson's[2] potassium coumarin product. These and the similar ethoxy derivatives were carefully investigated by Perkin and the results communicated in a later paper,[3] together with a discussion of this peculiar case of isomerism. Perkin notes the resemblance between these and fumaric and maleic acids, as Baeyer had also done, and observes that, according to van't Hoff's hypothesis, there should be two stereomeric coumaric acids. The chemical behavior of these acids led him, however, to believe that the cause of the isomerism in question is not connected with the unsaturated carbon atoms, simply concluding that "These facts would seem to indicate that in the α-compounds the groups, or some of them, contained in the molecules are *farther apart* than in the β-compounds."

In 1882 Roser[4] suggested his now well-known structural explanation of the isomerism of maleic and fumaric acids and stated that the isomerism in the coumaric acid series might possibly be explained by analogous structures. In the following year one of us[5] found that salicylresorcinolic ether unites with sodium hydroxide to form the compound,



[1] J. Chem. Soc., 31, 417.
[2] *Ibid.*, 28, 850.
[3] *Ibid.*, 39, 409.
[4] Ber. d. chem. Ges., 15, 2348.
[5] Michael: This Journal, 5, 93.

and, assuming similar constitutions for Williamson's sodium derivative of coumarin,[1] he explained the isomerism of the alkylcoumarinic (I.) and alkylcoumaric acids (II.) in the following manner :



II. $CH_3OC_6H_4CHO + (CH_3CO)_2O = CH_3OC_6H_4CH : CHCOOH + CH_3COOH.$

J. Wislicenus[2] revived the van 't Hoff explanation for these and other cinnamic acid derivatives, but one of us[3] shortly

[1] J. Chem. Soc., **28**, 1850.

[2] Räuml. Anord. u. s. w., p. 53.

[3] Michael : J. prakt. Chem., [2], **38**, 15-27. The correct interpretation of the isomerism in the substituted unsaturated monobasic acids, and the first experimental proof that 2 isomers exist having the same structural constitution, as has been assumed by van 't Hoff, was given by me in 1886. It was the impossibility of reconciling my results in the cinnamic acid series with the conclusions obtained by applying the van 't Hoff hypotheses to these substances that mainly led me to my supposed conservative attitude. The further testing of the matter has clearly demonstrated how fruitless are all these immature stereomeric speculations. Indeed, the confused condition of the theory in organic chemistry is largely due to their pernicious influence. Wislicenus, in his endeavor to make experiment conform with his theoretical views, reversed the position of the halogen atoms in the monohalogen cinnamic acids, which I had previously proved experimentally. Two years later (Ann. Chem. (Liebig), **248**, 354 ; cf. Michael : J. prakt. Chem., [2], **40**, 42), although nothing new in the subject had been published except my criticism of his views, he discarded his own and accepted my classification. It is true, that in this paper he stated that the conditions of isomerism in the cinnamic series are the same as in the crotonic series, but in doing this he simply tardily acquiesced in the conclusions which I had drawn several years previously from my researches. After almost 20 years we are facing the stubborn fact that the conclusions which Wislicenus drew by a systematic application of the van 't Hoff hypothesis are, without exception, absolutely untenable, and that our knowledge of the intramolecular atomic grouping consists largely of a collection of unproved and, among themselves, mainly contradictory assumptions. We do know now, however (*vide* Ber. d. chem. Ges., **34**, 3646 ; **39**, 203), that the van 't Hoff hypothesis no longer gives the correct number of isomers, and that it cannot be safely used in any reaction which involves a simultaneous chemical change on 2 carbon atoms in the molecules. A. M.

afterwards showed that the configurations given by Wislicenus to these substances led to a maze of astonishing contradictions.

This case of isomerism is particularly noticeable, in that neither of the above explanations may be said to offer a comprehensive solution of all the facts we know about these acids. We shall here discuss some of the more marked divergencies between the theoretical conceptions and the actual chemical behavior of these substances.

Compounds of the fumaric acid type, when heated, if they can pass over by loss of water into dehydrated ring products, show a tendency toward such a change, which change necessarily implies a conversion into the maleic form. Now the fumaroid coumaric acid is exceedingly stable toward heat, even when the temperature is raised to a point where decomposition sets in. It simply undergoes a retrogressive change without the formation of any coumarin. On the other hand, Fittig and Ebert[1] have shown that it is only necessary to allow coumaric acid to stand at the ordinary temperature with saturated hydrobromic acid to convert it completely into coumarin; that is, a reagent that ordinarily transforms a maleic into a fumaric modification in this case induces the reverse change. It is possible, however, that this absence of harmony between chemical cause and stereomeric effect may be more apparent than real, for one of us[2] has shown that the usual relation between physical and chemical properties is actually reversed in the case of cinnamic acid. For instance, ordinary cinnamic acid, which is wholly fumaroid in its physical properties, gives, primarily, addition products which are not fumaroid but malenoid in character. If, then, the closely allied cinnamic acid undergoes a chemical change by the addition of hydrobromic acid, the primary tendency may be in the direction of forming a malenoid substance.

Morgan and Micklethwait[3] have isolated a coumarin platinum chloride, $4C_9H_6O_2.H_2PtCl_4.4H_2O$. This indicates that coumarin and hydrobromic acid unite to form a "molecular compound"

[1] Ann. Chem. (Liebig), **226**, 352.
[2] Michael: Ber. d. chem. Ges., **34**, 3644.
[3] J. Chem. Soc., **89**, 863.

and not to form a brommellilotic acid. If the latter reaction took place, the lactone formation might be explained according to Wislicenus, *i. e.*, by rotation of the saturated configuration and elimination, first of water, then of hydrobromic acid. This principle, however, as a basis for stereomeric transformations has been given up, and to-day scarcely merits serious consideration. That it cannot be used in the present case follows from the experiments of Fittig and Hochstetter, who have shown that the stable saturated mellilotic acid is converted into its lactone at ordinary temperatures by hydrobromic acid.

Hjelt[1] has shown that coumaric acid does not exist in the free state even in the presence of water, going over into coumarin with surprising facility. On the other hand, Fittig and Hochstetter[2] found that the corresponding saturated compound undergoes the lactone condensation with great difficulty. This difference has been explained stereomerically,[3] inasmuch as in coumaric acid the position of the hydroxyl and carboxyl groups are fixed by the unsaturated carbon atoms, while in the saturated configurations these groups are in a condition of gyration and hence a position favorable to the conversion occurs in certain periods of the revolution. This is one of the many stereomeric explanations which are widely accepted, but which will not bear a critical examination. If the ease of the lactone formation were solely dependent on such a condition, at the moment when the interested groups were in a proper juxtaposition the condensation process should go on with readiness. Since such a gyratory motion must be assumed to be extremely rapid, it follows that the difference between the extents of lactone formation of coumaric and mellilotic acids can be only one of degree. This explanation, therefore, fails utterly in explaining the non-existence of coumaric acid and the stability of its reduction product.

One of us[4] has shown that the stereomeric explanation put forward by J. Wislicenus,[5] for the formation of lactones, is un-

[1] Ber. d. chem. Ges., **27**, 3331.
[2] Ann. Chem. (Liebig), **226**, 357.
[3] Harries, Meyer u. Jacobson, Lehrb. II., p. 674.
[4] Michael: J. prakt. Chem., **60**, 338.
[5] Räuml. Anord, etc., p. 68.

tenable and has pointed out that the process is really an intramolecular esterization, proceeding the more easily the less resistance there is in the molecule to the formation of the ring, and the recent investigations of Petrenko-Kritschenko and Konschin strongly confirm his view.[1] It is evident, therefore, that any change in the system which would facilitate esterization would bring about a more facile lactonization. Now mineral acids show such a catalytic effect to a marked degree and, consequently, it is not surprising that hydrobromic acid should favor the lactone formation in the above instances. Moreover, any chemical change in the structure of the side chain in mellilotic acid which accelerates the interaction between the hydroxyl and carboxyl groups must necessarily tend towards inducing easier lactonization. Such a change occurs with the unsaturation of the carbon atoms. This involves a greater accumulation of free energy on the carboxyl group, the fulcrum in the esterization process.

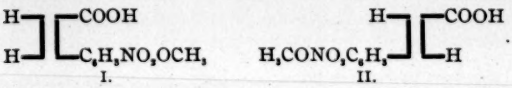
There is, indeed, an investigation in the fatty series which seems to point to the existence of stereomeric hydroxy acids resembling coumaric and coumarinic acids. Zelinsky,[2] by treating the addition product of hydrocyanic acid and acetylacetone with hydrochloric acid, obtained a monolactone of dimethyldihydroxyglutaric acid, which, on distillation, passed over into the dilactone. The lactonic acid, when heated with barium hydroxide, assimilates water and gives the salt of a dihydroxy acid, which, in the free state, spontaneously dehydrates into the original lactonic acid, while the dilactone, by a similar treatment, gave a stable dihydroxy acid. Zelinsky assumes that the stable form is the racemic modification, while the unstable form is optically active. It is, however, difficult to understand how any material change in the intramolecular gyration can be caused by racemization. This instance obviously offers no support to the Harries stereomeric explanation in the aromatic acids. It is to be regretted that this interesting subject has not been further investigated, as the assumptions of Zelinsky in regard to the constitution of

[1] Ann. Chem. (Liebig), 342, 53.
[2] Ber. d. chem. Ges., 24, 4006.

these products cannot be considered to be definitely established.[1] *Vide* also Rupe and Ronus.[2]

An interesting contribution to this subject was made by v. Miller and Kinkelin,[3] in a research on the mononitro substitution products of the coumaric acid derivatives. They found that *o*-nitrocoumaric acid, in contrast with coumaric acid itself, is capable of free existence. This fact is, however, explicable from either of the above points of view. The increased stability of the $C(OH)_2$ group, when the carbon atom is subjected to strong negative influences, is a characteristic property of the grouping; on the other hand, the more negative character a carbinol assumes, the less easily it unites with an acid to form an ester. In the further observation, however, that dimethyl *o*-nitrocoumarinate, on being warmed with sodium carbonate and alcohol, is completely saponified, *i. e.* goes over into *o*-nitrocoumarinic acid, while dimethyl *o*-nitrocoumarate, under similar treatment, yields *o*-nitromethoxycinnamic acid, which even continued boiling with alcoholic alkali but slowly converts into the hydroxy acid, is undoubtedly found to be a very serious argument against the stereomeric explanation. That the introduction of a nitro group into the ortho position in anisol derivatives renders the methoxy group somewhat more susceptible to saponification is easily understood from a theoretical point of view and has, indeed, been shown to be the case in several instances, but this grouping occurs in both the acids, and the marked contrast in their behavior towards alkalies cannot, therefore, be due to the influence of the nitro group alone.

Harries[3] has endeavored to bring the stereomeric explanation into accord with these facts. The configuration of *o*-nitromethoxycinnamic acid (I.) and its isomer (II.) are:



I. II.

[1] Ber. d. chem. Ges., **22**, 1705.
[2] *Ibid.*, **34**, 2191.
[3] Meyer u. Jacobson, Lehrb., II., p. 674.

Harries directs attention to the fact that in I. the methoxy group is not only subjected to the action of the nitro group, but, much more than in II., to the negative influence of the carboxyl group. Harries, therefore, concludes that the relative case of saponification of coumarinic acid is due to this difference and that the property agrees with the configuration of the compound. This is an argument which J. Wislicenus[1] frequently used in his speculations and which one of us,[2] years ago, showed to be based on fallacious reasoning. It is obvious that the first product formed when an acid and a base come in chemical contact must be a salt; therefore, it is no longer a question of the negative influence of the carboxyl group, but rather of the neutralized sodium derivative. Indeed, if we are to go back to known analogous instances, it may be safely stated that proximity of COONa should *increase* the resistance of the methoxy group to such a chemical change. In speculations on spacial influence it has been generally overlooked that such an influence is necessarily of a mutual character between the atoms or groups concerned. This is very noticeable in the present case; indeed, this point of view affords an explanation of some hitherto unexplained properties of phenolic derivatives. Thus, while salicylic acid, in aqueous solution, has a greater avidity than either the meta or para isomer,[3] it acts towards aniline blue as a monobasic acid, while the para isomer exhibits the behavior of a dibasic acid.[4] Again, the heat of neutralization of the 3 hydroxybenzoic acids, when treated with sodium hydroxide in molecular proportions, is practically identical. The addition of a second molecule of alkali gives a further evolution of 9.2 cal. with the 2 isomers of salicylic acid, but only 1 cal. with salicylic acid itself, so that it is doubtful if the disodium derivative can exist in the presence of water.[5] This relationship is also shown with other reagents. Thus, dry salicylic acid absorbs only 1 molecule of ammonia, while the meta and para acids unite with double

[1] Ann. Chem. (Liebig), **248**, 347.
[2] Michael: J. prakt. Chem., **40**, 37.
[3] Ostwald: *Ibid.*, [2], **32**, 345.
[4] Engel: Ann. Chim. Phys., [6], **8**, 573.
[5] Berthelot and Werner: *Ibid.*, [6], **7**, 146.

that amount. It also extends to the esters of the acids, as has been shown recently in this laboratory, while studying their behavior towards bases and other reagents. The explanation of these facts is obvious. Benzoic acid is a weak acid and, therefore, incapable of using up the positive energy of so strong a metal as sodium. For this reason, the more intimate the relationship of the second negative group, the hydroxyl, to the metal, the more complete must be the conversion of the residual negative energy in the molecule into bound energy or heat.

While the stereomeric explanation of Harries for the behavior of the nitro esters towards alkalies is untenable, it cannot be denied that the structural explanation of the isomerism is, in this respect, in good agreement with the facts.[1]

Recently Borsche[2] has endeavored to settle this question experimentally in a new manner. He starts from the point of view that according to the structural explanation coumarinic acid is a phenyl ester, while stereometrically considered it is a phenol. Now, as diazobenzene chloride is without action on the first group of substances, but yields azo derivatives with the latter, Borsche believes that this reagent may be used to decide the question. He found that potassium coumarinate and diazobenzene chloride give benzeneazocoumarin and, therefore, concludes that the stereomeric configuration has been proved in a conclusive manner. This conclusion is, however, based on very imperfect reasoning. The primary action of sodium phenolate on diazobenzene chloride is of an additive nature:[3]

$$C_6H_5NClN + C_6H_5ONa = C_6H_5\overset{\overset{Cl}{|}}{\underset{\underset{Na}{|}}{N}} : NOC_6H_5.$$

This product immediately decomposes into salt and

$$C_6H_5NNOC_6H_5,$$

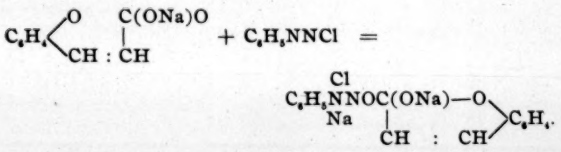
but, as the reaction takes place in the presence of an alkali and

[1] v. Miller and Kinkelin: Ber. d. chem. Ges., **22**, 1714.
[2] *Ibid.*, **37**, 346.
[3] Michael: *Ibid.*, **37**, 2098.

the new organic product has, within itself, the elements of instability, *i. e.*, an accumulation of negative atoms plus the possibility of an easy rearrangement to form a compound of a much more acidic nature than phenol, an intramolecular rearrangement does take place :[1]

$$C_6H_5NNOC_6H_5 + KOH = C_6H_5N : NC_6H_5OK + H_2O.$$

It is evident that a neutral phenyl ester could not form an addition product with diazobenzene chloride, but, and it is at this point that Borsche makes a mistake in his argument, there is no reason why such a basic compound as sodium coumarinate should not do so :



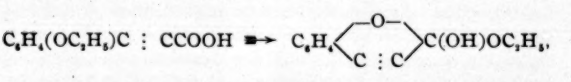
There exist, furthermore, the same conditions for the decomposition and rearrangement of the addition product into an azo derivative as when a phenolate is used.

It cannot be said, therefore, that the question whether coumaric and coumarinic acids are spacial or structural isomers has been conclusively settled, but there can be no doubt that spacial modifications of the hydroxycinnamic acids are capable of existence. Consequently, if the method used in preparing allocinnamic acid from cinnamic acid were employed with ethyl coumaric acid, the identity or non-identity of the product with ethylcoumarinic acid would be an argument in favor of one or the other view.

Cinnamic acid has been changed into allocinnamic acid by converting it into phenylpropiolic acid, adding hydrobromic acid to this[2] and reducing the bromcinnamic acid, m. p. 159°.[3] A similar series of manipulations with ethylcoumaric acid was

[1] Cf. Dieckmann : Ber. d. chem. Ges., **37**, 3370, 4627. Michael : *Ibid.*, **38**, 22.
[2] Michael and Brown : *Ibid.*, **19**, 1378 ; **20**, 550.
[3] Liebermann and Scholtz : *Ibid.*, **28**, 950.

found to yield an acid which proved identical with ***ethylcoumarinic acid.*** This is, indeed, a strong argument in favor of considering the relation between these acids as being similar to that existing between the stereomeric cinnamic acids. A rearrangement of the ethoxyphenylpropiolic acid under the conditions of the experiment into a lactone derivative,



is excluded. Besides, if it did take place, the next step in the process would not have been the formation of a bromethoxycinnamic acid but bromcoumarin. Incidentally, the question was examined whether an acid corresponding to isocinnamic acid[1] is formed in the reduction of *o*-ethoxy-β-bromallocinnamic acid. We were, however, unable to discover any indication of its formation.

Preparation of Ethylcoumarinic and Ethylcoumaric Acids.[2]

These isomeric acids were first prepared by Perkin,[3] who called them the α- and β-ethylcoumaric acids, respectively. Later, Ebert[4] devised convenient methods for their preparation, which Claus,[5] working afterwards in the same laboratory, also employed. But, strange to say, the β- or ethylcoumaric acid is best prepared by the method which Ebert gives for the preparation of the α-acid. According to his directions, coumarin (1 mol.) is dissolved in an ***absolute*** alcoholic solution of sodium alcoholate (2 mols.), and to this ethyl iodide (1 mol.) is added and the mixture digested for 3 hours. Ebert obtained, in this way, a good yield of ethylcoumarinic acid, m. p. 103°. We invariably obtained instead ethylcoumaric acid, m. p. 133°. Finally, influenced by the fact that Perkin employed an aqueous alcoholic solution of sodium hydroxide in his method of preparation, we substituted 96 per cent alcohol

[1] Erlenmeyer, sen: Ann. Chem. (Liebig), **287**, 21. Michael: Ber. d. chem. Ges., **34**, 3640; **36**, 900. Erlenmeyer, jun: *Ibid.*, **37**, 3361; **38**, 837.

[2] This work was done in the winter of 1901.

[3] J. Chem. Soc., **39**, 412.

[4] Ann. Chem. (Liebig), **216**, 142 ff.

[5] *Ibid.*, **269**, 2.

for the absolute alcohol of Ebert's directions. A good yield of ethylcoumarinic acid was thereby obtained. Thus, 6 grams of coumarin, 1.9 grams of sodium, 6.6 grams of ethyl iodide and 50 cc. of 96 per cent alcohol were digested for 3 hours on the water-bath, the product was evaporated to dryness, water was added and the whole shaken with ether to remove the neutral oil. The aqueous solution was warmed, then cooled and acidified. The precipitate dissolved completely in cold sodium carbonate, showing that all of the coumarin had been converted into an acid. The melting point of the acid, without recrystallization, was 102°–103°; weight 4 grams. The ether extract was saponified with alcoholic potassium hydroxide and yielded 3.3 grams more of an acid melting at 95°–97°. The total yield was 7.3 grams, the theoretical yield being 7.9 grams. It is, therefore, very probable that Ebert used an "absolute" alcohol which was not absolute. The ready conversion of coumarin into coumaric acid by sodium alcoholate is further evidenced by the impossibility of Ebert's method as given (cf. p. 579).

Obviously then, by simply employing either an absolute or a 96 per cent alcohol, one can prepare, in the first place, the high-melting ethylcoumaric, or, in the second case, the low-melting ethylcoumarinic acid, and each in excellent yield.

It was evident, in the above experiment, that small amounts of diethyl ester were formed, although coumarin and ethyl iodide were used in molecular proportions.

Preparation of Pure Ethyl Ethylcoumarate.

The ester, similarly to the acid, may be obtained directly from coumarin, sodium alcoholate and ethyl iodide, by using 2 molecules of ethyl iodide. Some experiments, however, indicated that an ester free from its isomeric ester was not obtained in this way. Thus, 8 grams of coumarin, 17.1 grams of ethyl iodide, 2.5 grams of sodium and 85 cc. of absolute alcohol were taken; 8.9 grams of an ester, boiling at 165°–173° (10 mm.), were obtained. When a relatively smaller proportion of alcohol was used, and a more complete conversion of lower-melting into higher-melting isomer secured, the

resulting ester was purer. Thus, 40 grams of coumarin, corresponding amounts of ethyl iodide and sodium, and 300 cc. of absolute alcohol, yielded 53 grams of ester boiling at 172°–174° (11 mm.). The attempt was made to isolate some of this low-melting isomer by using a larger proportion of alcohol and shortening the time of digestion. A mixture of 8 grams of coumarin, 17 grams of ethyl iodide, 2.5 grams of sodium and 100 cc. of absolute alcohol was digested for 3 hours, the alcohol was evaporated off and the neutral oil extracted with ether. The ester thus obtained yielded an acid which, when recrystallized, melted at 133°–134° and weighed 7 grams. From the aqueous solution, on the other hand, an acid was obtained which, after recrystallization from petroleum ether, melted at 102°–104° and weighed 1 gram. The low-melting acid was undoubtedly present, and there can, therefore, be no question but that some ethyl coumarinate was formed, in spite of the purity of the acid derived from it.

To remove the lower-boiling isomer, the crude product was saponified with boiling, concentrated, alcoholic potassium hydroxide and then boiled for 0.5 hour with a dilute aqueous solution of hydrochloric acid, which treatment converted all the low-melting isomer into higher-melting.[1] This resulting product was then converted into its ethyl ester by a 7–8 hours' digestion with absolute alcohol and a small quantity of sulphuric acid. There was very little loss in the process, and the resulting ester all distilled over at practically the same temperature. One sample came over at 176°–176°.5 (12 mm.); another at 173°–174° (11 mm.).

Addition of Bromine to Ethylcoumarinic and Ethylcoumaric Acids and to the Ethyl Ethylcoumarate.

Perkin,[2] on treating methylcoumaric and methylcoumarinic acids with bromine, obtained a different dibromide from each. Ebert,[3] on the other hand, found that the isomeric ethyl derivatives gave the same dibromide, and repeating the experiments of Perkin, could detect no difference between the di-

[1] Perkin : J. Chem. Soc., 39, 409.
[2] *Ibid.*, 39, 420.
[3] *Loc. cit.* p. 157.

bromide obtained from the methyl acids. We prepared the dibromide of ethylcoumaric acid by adding bromine to the acid, each in carbon bisulphide solution and in the sunlight. The resulting acid was identical with that obtained by Ebert, melting at 155°–156°. The dibromide of ethylcoumarinic acid was prepared in the same way, except that every precaution was taken to prevent the transformation of a low-melting into a high-melting isomer. The addition was carried on in a dark room at a temperature of 18°, and the bromine was added very slowly. Small, hard, colorless crystals were left after spontaneous evaporation of the solvent in the dark. After digesting the crystals with a little carbon tetrachloride, to remove any unchanged acid, the dried substance melted at 156°, with decomposition. The following determinations of its solubility in chloroform and carbon bisulphide, at 22°, were made:

Chloroform: 6.84 grams of solution contained 0.371 gram dibromide = 1 part of dibromide in 17.4 parts of chloroform; or in 100 parts of solution there were 5.4 parts of dibromide.

Carbon bisulphide: 8.46 grams of solution contained 0.111 gram dibromide = 1 part of dibromide in 75.6 parts of carbon bisulphide; or in 100 parts of solution there were 1.3 parts of dibromide. Ebert found the solubility to be 1.03 parts in 100.[1] These results, therefore, confirm Ebert's conclusion that the addition of bromine to ethylcoumaric and to ethylcoumarinic acid leads to the formation of the same dibromide.

The addition of bromine to the ethyl ethylcoumarate was carried out in the manner described by Perkin, except that the bromine was added only so long as decoloration took place quickly, which point was reached when about 1.9 atoms of bromine had been used. A very small quantity of hydrobromic acid was given off, indicating, perhaps, a slight substitution in the benzene nucleus. To obviate this as much as possible, the addition was always performed in diffused light, the solution of bromine in the carbon bisulphide was made dilute, the mixture kept cold and, as stated above, the ester was always kept in excess. The ease with which substitution takes place in the ring in these compounds is illustrated by the

[1] *Loc. cit.*, p. 159.

ready formation of the tri- and tetrabromides of ethylcoumaric and ethylcoumarinic acids.[1]

Preparation of Ethoxyphenylpropiolic Acid.

The preparation of a propiolic derivative from the dibromide of ethylcoumaric acid apparently offered little difficulty, since Perkin[1] had prepared methoxyphenylpropiolic acid and Claus[2] ethoxyphenylpropiolic acid itself in this way. Perkin removed the bromine in two stages, obtaining a monobrom acid by first rubbing the dibromide into a paste with a 50 per cent potassium hydroxide solution and then boiling the acid with alkalies. Following these directions, we invariably obtained an oil, which was insoluble in alkalies, perhaps ethoxybromstyrol or ethoxyphenylacetylene, as the chief product of the reaction, while only small quantities of the monobrom acid were found. Different alkalies in various relative proportions, at room temperature and at 0° were then tried, but without material improvement of the yield. Claus digested the dibromide immediately with boiling, concentrated potassium hydroxide and obtained a 50 per cent yield of ethoxyphenylpropiolic acid. We were unable to prepare, by this method, even after prolonged digestion with the alkali, an acid which would not give a test for halogen with copper oxide. Finally, good results were obtained by adding the ester dissolved, in a little alcohol, directly to a strong, boiling solution of alcoholic potassium hydroxide and digesting the mixture for about 2 hours.

Even after such drastic treatment, followed by several recrystallizations, the final product gave the test for halogen. This may be due either to the formation of substitution products containing bromine in the benzene nucleus, in which case the bromine would not have been removed by the above treatment, or, if the monobromide of the lower-melting isomer retains its bromine with the same tenacity as does the closely related, lower melting α-monobromcinnamic acid,[3] its presence would account for the persistence of the bromine in the product. The latter possibility, however, was eliminated by the

[1] *Vide* Perkin, *Loc. cit.*
[2] *Loc. cit.*
[3] Michael and Whitehorne: Ber. d. chem. Ges., 34, 3647.

method employed in the preparation of the ester. The precautions taken to prevent substitution in the ring are mentioned above.

Our attempts to remove this trace of bromine by recrystallization proved unsuccessful. The acid may be crystallized from water, carbon bisulphide and benzene, but it is sparingly soluble in these solvents and the product is freed from the bromine in this way with difficulty. We found that conversion of the acid into the calcium salt, digestion with a small amount of 50–60 per cent alcohol and reconversion into the acid, gave the best results. Samples of an acid, which repeated recrystallization from benzene and water had failed to purify, were shown to be free from halogen after a single treatment of this kind. The acid was finally recrystallized from an approximately 30 per cent mixture of acetic acid and water, which treatment, however, is accompanied with considerable loss.

The yield of crude acid was usually good, amounting to from 75–90 per cent of the theory. The yield of pure acid was never greater than 50 per cent, the chief loss occurring in the final recrystallization. Pure potassium hydroxide and alcohol should be used for the digestion, otherwise the resulting acid will only solidify after a long time. Prolonged digestion, too, decreases the purity of the product. The melting-point of the acid given by Ebert is 114°. Our purest samples melted at 115°.5–116°.

Action of Hydrobromic Acid on Ethoxyphenylpropiolic Acid.

Nine and eight-tenths grams of *o*-ethoxyphenylpropiolic acid were added to 85 grams of fuming hydrobromic acid, in a bath of ice water. After standing over night, the mixture was filtered, and the precipitate washed with ice water. The product of the reaction was dissolved in warm, 70 per cent alcohol, and small quantities of alcohol were added until the acid came down crystalline instead of as an oil. The first crop of crystals weighed 7.8 grams, the second 2.5 grams. They melted at 119°–119°.5.

The product is easily soluble in alcohol, ether, acetic acid and hot carbon tetrachloride, slightly in cold carbon tetrachlo-

ride and difficultly soluble in water. After recrystallizing from acetic acid once and from carbon tetrachloride twice, it melted at 120°. Analysis:

0.1100 gram bromide gave 0.0768 gram AgBr.

	Calculated for $C_{11}H_{13}O_3Br$.	Found.
Br	29.72	29.50

It is, therefore, ethylbromcoumaric acid, with the bromine undoubtedly in the β-position to the carboxyl group.

The filtrate from the crude ethylbromcoumaric acid was allowed to stand several days and then diluted with water. A yellowish precipitate was obtained, weighing but a few tenths of a gram, which was difficultly soluble in carbon bisulphide and carbon tetrachloride, chloroform, benzene and ligroin; somewhat soluble in hot water, easily in alcohol, acetic acid and especially soluble in acetone.

A sample of this product was recrystallized three times from boiling water. Small, yellowish white, needle-shaped crystals were obtained, which contained no halogen. They were again recrystallized from a mixture of acetone and ligroin, b. p. 110°–120°. The greater part of the acetone was then driven off by heating, whereupon the substance separated out in fine, white needles. It melts at 211°–212°.5 and, since it dissolves in alkalies, must be acidic in character. The solutions in alkalies thus obtained were colorless and the substance cannot, therefore, be coumaric acid. Analysis:

	Calculated for $C_{10}H_{11}O_3$.	Found.
C	67.00	67.07
H	6.20	6.53
O	26.80	26.40

These results correspond, however, to no substance which might be expected in the reactions.

The Reduction of β-Bromalloethylcoumaric Acid.

The reduction of β-bromallocinnamic acid to allocinnamic acid is best effected by means of zinc dust suspended in alcoholic solution of the acid, as described by Liebermann and

Scholtz.[1] The product of the reactions is a mixture, consisting mainly of the zinc salt of allocinnamic acid, some ordinary cinnamic acid and of a very low melting acid.

The allo acid is removed by taking advantage of the marked insolubility of its aniline salt in ligroin. Erlenmeyer sen.[2] isolated the iso acid by fractional precipitation and recrystallization from ligroin; Michael and Whitehorne,[3] by means of the different solubilities of the barium salts of the 3 acids in methyl alcohol.

Since the reduction of bromalloethylcoumaric acid might lead to a similar mixture of isomeric acids, experiments were carried out to see whether the methods of separation employed with the mixtures of the cinnamic acids could be used here. The action of aniline on ethylcoumaric and ethylcoumarinic acids was studied and the solubilities of the barium and calcium salts of these acids in water, ethyl alcohol and methyl alcohol were determined. The solubilities of the barium and calcium salts of ethylmellilotic acid, or hydroethylcoumaric acid, in the same solvents were also determined; since Michael and Garner[4] have concluded that the isocinnamic acid, obtained by the reduction of the β-brom acid, may be a mixture of allocinnamic acid and hydrocinnamic acid.

Aniline, in benzene solution, has no apparent action on ethylcoumaric or ethylcoumarinic acids, either at room temperature or at 100°.

For the solubility determinations, the barium and calcium salts were prepared by digestion of the acids with pure barium and calcium carbonates. Ethylmellilotic acid was prepared from ethylcoumaric acid by reduction with sodium amalgam. The salts were recrystallized either from water or alcohol. The temperature was allowed to vary between 20° and 24°, since great accuracy was not necessary.

It should be remarked that supersaturated solutions of these salts are easily formed, especially if they are in an amorphous condition, such for instance as a gummy residue, obtained by

[1] Ber. d. chem. Ges., **28**, 950.
[2] Ann. Chem. (Liebig), **287**, 5.
[3] Ber. d. chem. Ges., **34**, 3648.
[4] *Ibid.*, **36**, 900.

evaporating the solution of a salt in a solvent in which the salt is very soluble.

	Solubility of the barium salts of Ethylcoumarinic acid.	Ethylcoumaric acid.	Ethylmellilotic acid.
In water	(1) 2.7	(1) 290	(1) 18.6
	(2) 2.8	(2) 226	(2) 19.9
Methyl alcohol	(1) 414	(1) 30.4	(1) 31.4
	. . .	(2) 22.4	. . .
Ethyl alcohol	(1) 2137	(1) 259	(1) 104
	(2) 2327	(2) 110	(2) 86.3
	. . .	(3) 167	(3) 93.0
	Solubility of the calcium salts of Ethylcoumarinic acid.	Ethylcoumaric acid.	Ethylmellilotic acid.
In water	(1) 18.7	(1) 219	(1) 147
	(2) 31.7	. . .	. . .
Methyl alcohol	952	861	205
Ethyl alcohol	(1) 731	(1) 1641	1121
	(2) 1454	(2) 1892	. . .
	. . .	(3) 1846	. . .

The figures indicate parts by weight of solvent corresponding to a single part of solute.

It is evident that alternate treatment of the barium salts of ethylcoumaric, ethylcoumarinic and mellilotic acids, with water and alcohol, should offer a method of separation.

Four reduction experiments were carried through, with nearly identical results, using Liebermann's method. In the first of these experiments 8 grams of ethylbromcoumaric acid, 16 grams of zinc dust and 80 cc. of 96 per cent alcohol were taken. The mixture was digested for 6 hours on the water-bath. At frequent intervals samples of the mixture were removed and the zinc bromide determined, in order to ascertain the progress of the reaction. Since these tests showed that the reaction was complete within the first half hour, in our later experiments the period of digestion was shortened to an hour. The mixture was then diluted with an equal volume of water and evaporated to a small bulk; more water was added, the solution acidified and the acid extracted with ether. It softened at 75° and melted at 81°–97°, being evidently a mixture, apparently containing ethylcoumarinic acid, m. p. 103°.

It seemed advisable, therefore, to follow the method of separation suggested above, depending on the different solubilities of the barium salts of the ethyl derivatives of coumaric, coumarinic and mellilotic acids. The crude product was converted into the barium salts by prolonged digestion for 8–10 hours with barium carbonate, in water, at 70°. The resulting solution was filtered and the filtrate evaporated to dryness. The residue was then extracted with about 50 cc. of absolute alcohol, in which barium ethylcoumarinate is very insoluble. At first it goes into solution, but quickly comes down as a copious, white substance. The mixture was allowed to stand over night, to insure precise saturation, and then filtered. Two samples of the precipitate were dissolved in water, the solution acidified and the acid extracted with ether. As they melted between 99° and 102° they were evidently slightly impure ethylcoumarinic acid. The yield, too, was considerable. In this experiment the weight of the barium ethylcoumarinate was 6.8 grams, while in another, starting with the same amount of ethylbromcoumaric acid, 7.3 grams of barium salt were obtained, corresponding, respectively, to a yield of 80 and 90 per cent of ethylcoumarinic acid.

Ethylcoumarinic acid is, therefore, the main product of the reduction of β-ethylbromcoumaric acid by means of zinc dust in alcoholic solution.

The Existence of Isocoumaric Acid.

It remained to detect, if possible, the presence of an acid corresponding to the isocinnamic acid of Erlenmeyer and Michael and Whitehorne, this being the second object of the research. It was evident, from the purity of the ethylcoumarinic acid which had been isolated from the product of reduction in the above experiment, that the iso acid must, if present at all, be dissolved in the filtrate from the barium ethylcoumarinate. Further, from analogy with allobromcinnamic acid we also should expect that the reduction would lead to the formation of some of the high-melting isomer, or ethylcoumaric acid. The alcoholic filtrate from the barium ethylcoumarinate was evaporated to dryness and extracted

with about 10 cc. of water, in which barium ethylcoumarate had been found to be difficultly soluble. The mixture was allowed to stand over night and was then filtered. A portion of the gummy residue from the evaporation of this filtrate was dissolved in much water and acidified. The free acid was extracted with ether and dried, when it melted at 127°–132°. There can be no doubt but that it was fairly pure ethylcoumaric acid, m. p. 133°. The exact weight of the acid was not easy to determine because of its gummy nature, but it was approximately 0.3 gram, or 5 per cent of the total reduction product.

Any iso acid must have been dissolved in the filtrate from the barium ethylcoumarate. It would have been mixed, however, with as much barium ethylcoumarinate and ethylcoumarate as 50 cc. of absolute alcohol and 10 cc. water, in succession, would have dissolved. The filtrate was evaporated to dryness and the residue, amounting to about 0.3 gram, extracted with 5 cc. of each solvent, in succession, whereby some ethylcoumarinic and a little ethylcoumaric acid were further separated. The aqueous solution remaining from this last extraction was filtered and acidified. The precipitated acid was filtered off and dried. The melting points of samples of the acid thus extracted in the 4 reduction experiments were as follows:

(1) softened at 83°, ran at 87°, completely melted at 115°
(2) " " 82°, " " 92°, " " " 101°
(3) " " 79°, " " —— " " " 86°
(4) " " 80°, " " 94°, " " " 120°

The weight of the residue obtained from the reduction of 8 grams of ethylbromcoumaric acid varied between 0.1 and 0.2 grams, or 2–3 per cent of the total reduction product.

These melting points indicated that the residue was a mixture of ethylcoumaric and ethylcoumarinic acids. The results with the third portion, however, suggested that a still lower melting acid might be present. To be better able to judge regarding this possibility, the melting points of various mixtures of (1) ethylcoumaric and ethylcoumarinic acids, (2) ethylcoumaric and ethylmellilotic acids, (3) ethylcoumarinic and

ethylmellilotic acids were determined. These mixtures were prepared by dissolving the acids either in absolute methyl or ethyl alcohol and evaporating to dryness. The point at which the substance ran freely could be determined with the greatest accuracy of any. Ethylmellilotic acid was included because the presence of its analogue had been suspected among the reduction products of allocinnamic acid.[1]

Table I.—Mixtures of Ethylmellilotic and Ethylcoumaric Acids.

Weight of mixture. Gram.	Total weight of ethylcoumarinic acid added. Gram.	Percentage of ethylmellilotic acid.	Mixture. Softened.	Ran.	All melted.
0.4676		100			
0.5270	0.0594	88.7	62°	66°	74°
0.5687	0.1031	81.9	62°	70°	77°
0.6211	0.1575	74.6	60°	66°	70°
0.7221	0.2605	63.9	59°	61°.5	70°
0.8107	0.3511	56.7	60°	62°.5	70°
	Total weight of ethylmellilotic acid added.				
0.6373					
0.7108	0.0735	10.3	72°	86°	101°
0.8282	0.1951	23.3	63°	86°	96°
0.9044	0.2713	30.2	62°	71°	98°
1.0637	0.4326	40.6		64°.5	87°
1.1826	0.5535	46.8	60°	62°.5	82°
	Total weight of ethylcoumarinic acid.				
0.1044					
0.1070	0.0026	97.6	69°	77°.5	79°.5
0.1117	0.0093	91.7	61°	77°.5	78°
0.1160	0.0156	86.6	58°	69°	75°
0.1226	0.0242	80.3	61°	63°	65°
0.1276	0.0254	80.1	61°	64°.5	71°

[1] Liebermann: Ber. d. chem. Ges., **36**, 179. Michael and Garner: *Ibid.*, **36**, 907.

Table II.—Melting Points of Mixtures of Ethylcoumaric and Ethylcoumarinic Acids.

Weight of mixture. Gram.	Total weight of ethylcoumaric acid added. Gram.	Percentage ethylcoumaric acid.	Mixture. Softened.	Ran.	Completely melted.
0.2029		0.0			
0.2219	0.0190	8.58	83°.5	92°.5	100°.5
0.2385	0.0186	15.7	86°	91°	98°
0.2599	0.0234	23.2	83°	84°	91°
0.2725	0.0146	27.4	82°	84°	90°
0.3090	0.0385	36.9	81°	84°	101°
0.3726	0.0656	48.2	82°	85°.5	112°
	Total weight of ethylcoumarinic acid added.				
0.2444		100.0			
0.2518	0.0074	97.1	117°	128°	131°
0.2820	0.0302	86.7	102°	115°.5	127°
0.3020	0.0220	80.3	89°	115°	126°
0.3536	0.0536	68.0	83°	97°	126°
0.4044	0.0528	58.9	83°	89°	117°
0.4262	0.0738	49.6	84°	85°.5	107°

Melting Point of Mixture of Ethylcoumaric and Ethylmellilotic Acids.

Weight of mixture. Gram.	Total weight of ethylmellilotic acid added. Gram.	Percentage ethylmellilotic acid.	Mixture. Softened.	Ran.	Completely melted.
0.1817		0.0			
0.1950	0.0133	6.8	110°	126°	129°
0.2062	0.0265	12.8	117°	124°	129°
0.2283	0.0506	22.2	100°	118°	129°
0.2588	0.0831	32.1	75°	105°	118°
0.2841	0.1104	39.6	77°	95°	106°.5
0.3101	0.1384	44.6	71°	77°	114°
	Total weight of ethylcoumaric acid.				
0.1562		100.0			
0.1723	0.0161	90.7	72°	74°.5	76°.5
0.1887	0.0345	81.6	70°.5	72°	73°
0.2081	0.0559	73.2	70°.5	72°.5	95°
0.2422	0.0920	62.0	73°	86°	107°
0.2688	0.1206	55.2	75°	88°.5	110°
0.3077	0.1615	47.5	71°	96°.5	119°

When these results were plotted in the form of curves it is found that all the melting points of the above residues fit the melting point curve for mixtures of ethylcoumaric and ethylcoumarinic acids. The conclusion that the residue consisted of these 2 acids is thus confirmed, but it was desirable, if possible, to apply a more delicate test for the detection of ethylmellilotic acid. This available residue was too small and undoubtedly too impure to afford an analysis sufficiently accurate to distinguish between ethylcoumaric and ethylmellilotic acids. The action of potassium permanganate on a mixture of these two acids was tried, and although the unsaturated acid oxidized much more rapidly, the end point was so difficult to ascertain that the method was abandoned. The following experiments on the action of bromine vapor on ethylcoumaric, ethylcoumarinic and ethylmellilotic acids were carried out in the hope of obtaining some method of detecting small quantities of the ethylmellilotic acid in the presence of the other three.

Action of Bromine, in Excess, on Ethylcoumarinic, Ethylcoumaric and Ethylmellilotic Acids.

(1) *Ethylcoumarinic Acid.*—Samples of this acid were exposed to the action of bromine vapor in a desiccator, kept in the dark. After 24 hours the excess of bromine was allowed to diffuse into the air and the remainder removed by placing the product over sodium hydroxide and sulphuric acid, in a vacuum.

(1) 0.3579 gram acid increased 0.5239 gram, or 323.2 equivalents.

(2) 0.2370 gram acid increased 0.3535 gram, or 320.7 equivalents.

4 atoms of Br — 2 atoms H = 320 — 2 = 318 equivalents.

No further diminution in weight occurred even after prolonged standing over sodium hydroxide.

The solubilities of this bromide agree with those of the bromide derived from ethylcoumaric acid, although we did not succeed in recrystallizing it. The crude product softened at 142° and melted at 150°–152°. Analysis:

0.2062 gram substance yielded 0.2894 gram AgBr.

	Calculated for $C_6H_2Br_2OC_2H_5.C_2H_3Br_2COOH$.	Found.
Br	62.64	59.7

(2) *Ethylcoumaric Acid.*—Exposed over night to the action of bromine vapor, the substance increased in weight by an amount equivalent to between 3 and 4 atoms of bromine, and lost weight but very slightly on further exposure over sodium hydroxide. Protracted exposure to bromine vapor resulted in the addition of somewhat more than 4 atoms, but the product lost weight over sodium hydroxide until the increment of bromine corresponded to about 3.5 atoms. The addition product is very soluble in acetone, alcohol, ether, and carbon bisulphide; easily soluble in hot, less soluble in cold benzene, toluene and chloroform; somewhat soluble in hot ligroin, but decomposes more or less if the ligroin employed boils much above 100°. A sample was recrystallized from a mixture of acetone and ligroin, then several times from toluene and chloroform, when it melted at 183°–184°, with very slight decomposition. It crystallized from toluene and ligroin in thin, rhombic plates. Analysis:

0.2263 gram substance yielded 0.3374 gram AgBr.

	Calculated for $C_6H_2Br_2OC_2H_5.C_2H_3Br_2COOH$.	Found.
Br	62.64	63.45

The substance may be called α,β-dibrom-β-dibromethoxyphenylpropanic acid.

(3) *Ethylmellilotic Acid.*—The acid, when exposed to bromine vapor, is converted into a thick, red liquid. The increase in weight corresponds, roughly, to 4 atoms of bromine. However, on standing over sodium hydroxide the greater part of this bromine was given off and a steady loss in weight occurred.

It appears, then, that these 3 acids do not behave at all identically toward bromine vapor. While the 2 unsaturated acids form dry, powdery addition products, which are apparently mixtures of tri- and tetrabrom addition products, and which do not lose in weight on standing over sodium hydrox-

ide after the excess of bromine has been removed, ethylmellilotic acid forms a thick liquid which loses in weight indefinitely under these same conditions. It was found possible to detect, in this way, a small per cent of ethylmellilotic acid in mixtures of it with ethylcoumaric and ethylcoumarinic acids.

It follows, then, that if the final residue from the reduction experiment contained more than a small per cent of ethylmellilotic acid, the external appearance of the addition product with bromine, combined with a steady loss in weight on standing over sodium hydroxide would disclose the fact. A sample of the residue was, therefore, exposed over night to the action of bromine vapor. It yielded an addition product which was dry and powdery.

After treatment with bromine and 2 hours' standing over sodium hydroxide, 0.0678 gram of residue weighed 0.1731 gram; after standing 16 hours longer, it weighed 0.1733 gram. The increment equals 0.1053 gram, and corresponds to an equivalent increment of 297.2, or somewhat less than 4 atoms of bromine, as would be expected from a mixture of ethylcoumarinic and ethylcoumaric acids. As no loss in weight occurred we may conclude that certainly not more than minute quantities of ethylmellilotic acid could have been formed in the reduction.

Action of Four Equivalents of Bromine on Ethylcoumaric and Ethylcoumarinic Acids.

(1) *Ethylcoumarinic Acid.*—Three grams of pure, dry acid were dissolved in chloroform, and to the solution 4.5 grams, = 4 atoms, of bromine, also dissolved in chloroform, were added. The mixture was allowed to stand several days in the dark. Much hydrobromic acid was evolved and the solution finally became colorless, a considerable quantity of white crystals being deposited.

A small quantity of a thick, heavy, red liquid was also formed, which gave off fumes of hydrobromic acid on exposure to the air. The supernatant liquid was allowed to evaporate in the air and a residue was obtained, which appeared to be identical with the crystalline product. The crystals are very easily soluble in acetone and alcohol, quite soluble in boiling

toluene and rather difficultly soluble in chloroform, carbon tetrachloride and, especially, in ligroin. When crystallized from a mixture of acetone and ligroin, then from toluene and, finally, from chloroform, it melts at 182°–183°, with considerable decomposition. The crystals from the mixture of acetone and ligroin were short, slightly rhombic needles; from toluene they were small, colorless and nearly rectangular in shape. Analysis:

0.1621 gram substance yielded 0.2101 gram AgBr.

	Calculated for $C_6H_3BrOC_2H_3.C_3H_2Br_2COOH$.	Found.
Br	55.66	55.15

The substance may be called α,β-dibrom-β-bromethoxyphenylpropanic acid.

(2) *Ethylcoumaric Acid.*—Three grams of pure, dry acid were dissolved in chloroform, and to it 4.5 grams, or 4 equivalents of bromine, also dissolved in chloroform, were added. After standing several days the solution was still reddish in color, and no crystals had formed, though much hydrobromic acid had been given off. On evaporation a residue was left which proved to be about as soluble in carbon tetrachloride as it was in chloroform; otherwise it closely resembled in its solubilities the above tribrom compound of ethylcoumarinic acid. It gave gummy residues, however, from nearly every solvent, and could not be recrystallized.

To enable us to draw some conclusion relative to the composition of this residue it was treated with alkalies. One gram of the residue, dissolved in a little alcohol, was added to a boiling solution of 1.5 grams of sodium hydroxide in 15 cc. of alcohol, and the mixture was digested on the water-bath for 1.5 hours. The solution was then evaporated, the residue dissolved in water, an oily turbidity filtered off, and the filtrate acidified. The resulting flocculent precipitate was filtered off and dried. It crystallizes in needles and is easily soluble in acetone, alcohol, chloroform, carbon tetrachloride, carbon bisulphide and toluene; difficultly soluble in ligroin and water.

After 2 recrystallizations from toluene the substance melted at 134°–136°. Analysis:

0.0957 gram substance gave 0.0662 gram AgBr.

	Calculated for $C_6H_3BrOC_3H_5.C_2COOH$.	Found.
Br	29.50	29.44

This substance is, therefore, *o*-ethoxybromphenylpropiolic acid.

The formation of this monobrom acid showed that a bromine atom had entered into the benzene nucleus and that the above residue must have consisted principally of a tribrom derivative of ethylcoumaric acid, or *o*-ethoxybromphenyldibrompropionic acid. Further, it is significant, that its properties are decidedly different from those of the *o*-ethoxybromphenyldibrompropionic acid derived from ethylcoumarinic acid, although the possibility of stereoisomerism disappeared with the unsaturation.

Since, however, Perkin found that methylcoumaric and methylcoumarinic acids gave the same *o*-methoxybromphenyldibrompropionic acid, this indirect evidence of the dissimilarity of the corresponding products derived from the ethyl acids requires confirmation.

Addition of Chlorine to Ethylcoumarinic Acid.

Two grams of ethylcoumarinic acid were added to a sufficient quantity of a 9.2 per cent solution of chlorine, in carbon tetrachloride, to form a dichloride. The acid had previously been dissolved in dry carbon bisulphide and the addition was carried on in the dark. After standing 12 hours crystals had separated, and these were filtered off. They melted at 127°–128° and softened at 125°. They were easily soluble in alcohol, chloroform and hot carbon tetrachloride; somewhat soluble in ligroin and carbon bisulphide. After recrystallization from ligroin the substance melted at 130°–131°. Analysis:

0.1559 gram substance gave 0.1720 gram AgCl.

	Calculated for $C_6H_4OC_3H_5.C_2H_3ClCOOH$.	Found.
Cl	26.96	27.23

The Conversion of Coumarinic Derivatives into Their Coumaric Isomers.

Coumarin is converted into the sodium salt of coumaric acid by boiling with strong, aqueous sodium hydroxide,[1] more readily by boiling with a solution of sodium ethylate in absolute alcohol. Coumaric acid is reconverted into coumarin with so much difficulty that it would seem probable that the latter is the lactone of an allocoumaric acid. It seemed of interest, therefore, to subject ethylcoumarinic acid to the same treatment. Three-tenths gram of sodium was dissolved in 6 cc. of absolute alcohol, and to the solution 1 gram of pure ethylcoumarinic acid was added, and the mixture was digested in an oil-bath, at 120°, for 5 hours. The solution was then diluted with water, evaporated to dryness, the residue dissolved in water and acidified. The resulting acid, when dried, melted at 98°–100°. This experiment was repeated, except that 4 instead of 6 cc. of absolute alcohol were employed, whereupon the resulting acid melted at 99°–102°. It is evident that ethylcoumarinic acid is not affected by digestion with a solution of sodium in absolute alcohol.

Perkin[2] found that methylcoumarinic acid is converted into its isomer by boiling with dilute mineral acids. Ethylcoumarinic acid was found to be similarly changed. The conversion, however, is slow. Thus 0.5 gram of acid, after heating with 10 cc. of dilute hydrochloric acid for 1.25 hours, in an oil-bath, at 120°, melted between 104° and 122°, corresponding to about 75 per cent of ethylcoumaric acid (see table, p. 573). On the other hand, coumarin was quite unchanged by this treatment.[3]

Liebermann[4] has found that allocinnamic acid is converted rapidly into ordinary cinnamic acid by the action of iodine, dissolved in carbon bisulphide. This experiment was tried with ethylcoumarinic acid. One and one-half grams of the acid, m. p. 103°, were added to a solution of 3 grams of iodine in

[1] Delalande: Ann. Chem. (Liebig), **48**, 332. Perkin: J. Chem. Soc., **31**, 417. Fittig and Ebert: Ann. Chem. (Liebig), **216**, 142.

[2] *Loc. cit.*, p. 410.

[3] Delalande: *Loc. cit.*, p. 333.

[4] Ber. d. chem. Ges., **23**, 2512.

35 grams of carbon bisulphide, and the mixture digested for 4.5 hours on the water-bath. The iodine was removed by means of a strong solution of sodium thiosulphate and the colorless carbon bisulphide solution was then shaken with water and, finally, with an aqueous solution of potassium hydroxide. From the alkaline solution an acid was obtained which melted at 132°–133°, showing a complete conversion into ethylcoumaric acid.

For comparison, the effect of iodine on coumarin itself was tried. A quantity of coumarin, with 10 times its weight of water, was digested 2.5 hours with a solution of iodine in carbon bisulphide, without any change taking place.

It is also of interest that, although coumarin is rapidly converted into orthocoumarinate by boiling with a strong solution of sodium alcoholate in *absolute* alcohol, it is scarcely affected at all if a solution of the alcoholate in 96 per cent alcohol be employed. This fact agrees with the experience gained in the preparation of ethylcoumarinic acid, and may also explain the difficulty which Miller and Kinkelin[1] experienced in converting coumarin into coumaric acid.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

XII.—STUDIES ON THE SOILS OF THE NORTHERN PORTION OF THE GREAT PLAINS REGION: THE SECOND STEPPE.

By Frederick J. Alway.

Very little study has been devoted to the chemical and physical properties of the soils of the northern portion of the great plains region, better known as the Canadian Northwest. In the few investigations that have been conducted there, methods have been employed which are adapted to the humid climate of eastern Canada, but which are ill suited to the conditions that have produced the prairies and plains.

The commonly accepted explanation of the large yields of grain obtained in the Canadian Northwest is quite erroneous and obscures the value, to the agricultural interests of the

[1] Ber. d. chem. Ges., 22, 1714.

semi-arid portions of the United States, of the data contained in the annual reports of the Indian Head Experimental Farm, covering a period of 17 years.

The yield from a given area of crop depends upon the climate during the season of growth and upon the fertility of the soil, whether it is considered that the latter is due chiefly to its physical properties or to its store of readily available plant food. The different factors of climate are easily determined and their influence upon plant growth is very apparent, while the relative fertility of the soil can be ascertained only by measuring the crop yield under ideal climatic conditions, which differ for different soils. The climate of the second prairie steppe of Canada is distinguished from that of the prairie portions of the United States chiefly in its lower winter temperature, its somewhat longer summer days and its low precipitation, the rainfall occasionally amounting to less than 5 inches during the crop season. Eminent American and English chemists have advanced, or accepted, in explanation of the large yields of grain in this region, the theory that the frost penetrates to a great depth during the winter and, during the summer months, furnishes a constant supply of moisture to the growing grain. Sir Wm. Crookes[1] has made the statement that "The fertility of the Northwest Provinces of the Dominion of Canada is due to an exceptional and curious circumstance. In winter the ground freezes to a considerable depth. Wheat is sown in the spring, generally April, when the frozen ground has been thawed to a depth of 3 inches. Under the hot sun of the short summer the grain sprouts with surprising rapidity, partly because the grains are supplied with water from the thawing depths. The summer is too short to thaw the ground thoroughly, and gate posts or other dead wood extracted in the autumn are found still frozen at their lower ends." Storer[2] quotes, as an illustration of how melting ice may serve as a useful store of moisture in certain situations and for certain crops, in regard to Assiniboia, "that even in late July some of the soil still holds the winter's frost at a depth of several

[1] Presidential Address, British Assoc. Report, 1898, p. 8.
[2] Agriculture (7th ed.), Vol. I., p. 144.

feet below the surface. This underground layer of frozen earth is believed to explain the wonderful fertility of the soil, as the frost, in gradually coming to the surface during the summer months, creates a moisture which, meeting the warmth from above, forms a kind of natural hot bed. This moisture counteracts the scarcity of rain during the spring and summer and accounts for the grain being forced with such amazing rapidity after the late sowing."

Up to the present time this explanation seems to have passed without criticism. The soil of the prairie and of the grain fields does not remain frozen throughout the summer at any depth in ordinary years and, probably, in any year. The experimental data upon which this generalization is based will be published in another journal. The preponderating importance of the nature of the subsoil, rather than that of the surface soil, or of the depth to which the frost penetrates, has hitherto not been recognized.

At the southern boundary of Canada the region of plain and prairie extends from the 96th to the 114th meridian and "narrows rapidly northwards, by the encroachment of its eastern border, but continues as a great physical feature to the shore of the Arctic Ocean. Beyond the North Saskatchewan River, however, it loses its essentially prairie character and becomes, with limited exceptions, thickly covered with coniferous forest."[1] The Rocky mountains or bordering foothills form the western boundary of this interior continental plateau; the northeastern boundary is formed by the rocky plateau of the great Archaean nucleus of the continent. Two escarpments, which hold a northwest and a southeast course across the plains, form the eastern boundaries of the third and the second prairie levels or steppes, the more easterly of which overlooks the lowest or first steppe. The three prairie steppes differ in age, in the character of the superficial deposits and, to a considerable extent, in climate.

The first steppe, a large part of which is commonly known as the Red River Valley, extends from the Red River and

[1] Selwyn and Dawson: "Descriptive Sketch of the Physical Geography and Geology of the Dominion of Canada," 1884, p. 27.

Lake Winnipeg westward to the first escarpment which, in its different portions, passes under the designations—Pembina Mountain, Tiger Hills, Riding Mountain, Duck Mountain, Porcupine Hills and Pasquia Hills. This prairie level was covered, toward the close of the glacial period, by a large body of fresh water, named by Upham,[1] Lake Agassiz. The surface soil, which is of lacustral origin, consists of fine silty material over the greater portion of the steppe, the average height above the sea being about 800 feet. The Red River Valley of Minnesota and North Dakota forms a southward extension of this area. The soil of this valley, which is famous for its fertility, has been studied at the experiment stations of the 2 states mentioned. The attention of Lawes and Gilbert was drawn to the fertility of the Manitoba portion and they made analyses of samples from various localities. Some contributions to the chemistry of the soil of this steppe have since been made by Shutt.[2]

The second steppe extends from the first escarpment to the second, the Missouri Couteau. "It includes the whole eastern portion of the great plains, properly so-called, of Canada."[3] The average altitude of this prairie level is about 1600 feet. Its climate, like that of the first steppe, is characterized by warm summers, very cold winters and a low winter precipitation. The rainfall, which occurs chiefly during the growing season, is lighter than that of the first level. Considerable areas of the second steppe were covered by lakes at the time that Lake Agassiz occupied the lowest level, and in these deposits of silty material of varying thickness were formed.

The fertility of the soil of the second steppe is apparent to any one that visits the province of Saskatchewan at the close of a favorable crop season. It is a well-recognized fact, however, that in regions where the normal precipitation is very small, abundant crops are produced, even on very coarse sands, in those seasons during which the rainfall is unusually heavy and well distributed. Evidence that the soil of southern Sas-

[1] W. Upham: Lake Agassiz, U. S. Geol. Survey, 1895.
[2] Annual Reports Canada Expr. Farms.
[3] Selwyn and Dawson: *Loc. cit.*

katchewan is characterized by the ability to produce a high average yield of wheat, oats, barley and potatoes for many years in succession, without the application of any fertilizers, or even the growing of leguminous crops, is furnished by the annual reports of the Indian Head Experimental Farm, which has been maintained by the Canadian government since 1888. Experimental farms are maintained by the same government at 4 other places, Nappan in Nova Scotia, Ottawa in Ontario, Agassiz in British Columbia, and Brandon in Manitoba. The 3 represent humid climates with a heavy winter precipitation, while the farms at Brandon and Indian Head are in the region of very light winter precipitation. In illustration of the above-mentioned characteristics the yields of the 12 best adapted varieties of wheat, oats, barley and potatoes, during the past 4–9 years that they have been under trial at the 5 farms, where the conditions of experiment are similar, are given in Table I. The average yield of each of these 4 crops is higher at Indian Head than at any of the 4 other experimental farms. The yields of the same crops in 1901 are given in the table in illustration of the effect of a very favorable crop season at Indian Head. It is important to note that only in the case of peas, in addition to the 4 crops mentioned, does the Indian Head farm give heavy yields. The other crops indicated in the table, as well as hay, produce more heavily at each of the 4 other farms.

The soil of the Indian Head farm is typical of that of the greater portion of the second steppe. The surface soil consists in some places of boulder clay and in others of a lacustral deposit of clay overlying the till. In none of the fields on the farm, where borings were made by the writer, was the lacustral deposit found to exceed 3 feet in depth. The soil of the whole of the second steppe is of glacial origin, the till, which covers the underlying Cretaceous shales, varying in depth from a few feet in the vicinity of the Souris river to more than 200 feet over a great part of the area. The drift consists of an intimate mixture of the country rock, in a very finely divided condition, with powdered Devonian and Silurian limestones, together with material from the great Archaean

Table I.

Average yields of the best adapted varieties of various crops at the 5 Canadian Experimental Farms. Some of the varieties included in the averages have been under trial only 4 years, but most of them have been tested for 9 years.

Crop.	No. of varieties.	Average for the years 1895–1903.[1] Average for 5 farms.	Ottawa.	Nappan.	Brandon.	Indian Head.	Agassiz.	Average of the same number of varieties at Indian Head in 1901.[2]
Oats, bush. (34 lbs.)	12	76.2	64.5	77.2	88.5	94.5	67.5	132.8
Barley, 2-rowed, bush.	6	45.5	45.3	45.1	46.0	56.2	43.3	60.6
" 6-rowed, "	6	50.8	50.1	50.6	56.0	60.5	45.9	64.0
Spring wheat, "	12	34.3	28.0	36.9	35.9	42.2	34.9	63.2
Peas "	12	35.7	33.6	31.9	47.3	41.5	37.5	57.7
Maize, green, tons	6	19.4	23.1	18.8	19.6	14.6	22.9	25.2
Turnips, "	6	31.5	34.2	39.9	25.1	22.3	39.7	37.5
Mangels, "	6	31.7	39.1	38.0	31.1	22.6	34.3	29.3
Carrots, "	6	22.0	30.7	22.3	14.3	12.2	31.1	12.6
Sugar beets, "	4	24.5	28.8	27.2	19.4	11.2	17.0	27.7
Potatoes, bush.	12	377.9	399.2	387.0	395.3	433.6	371.0	620.5

[1] Bull. 48, Canad. Expr. Farms (1904).

[2] Bull. 39, Canad. Expr. Farms (1901).

area to the northeast. The gravel, stones and boulders are chiefly from the last-mentioned source, together with a limited number composed of limestone, these, probably, having been brought from the Palaeozoic belt separating the Cretaceous area from the Archaean.

Previous Analyses of Soils from the Second Steppe.

The only analyses of soils from this prairie level hitherto published are those by Shutt.[1] For purposes of comparison these are given.

Table II.—Analyses of Soils, Water-free, from the Northwest Territories.

	Moosomin. Surface.	Saltcoats. Surface.	Yorkton. Surface.	Yorkton. Subsoils.
Potash	0.36	0.34	0.49	0.42
Phosphoric acid	0.11	0.21	0.21	0.09
Lime	0.95	2.90	0.06	0.75
Nitrogen	0.48	0.57	0.50	0.13
Loss on ignition	11.79	13.57	14.01	8.18

The depth to which the samples were taken is not stated.

Chemical Analysis of Indian Head Soils.

The samples of soil, the chemical analysis of which is given in Table III., were secured by Mr. B. F. Reynolds on Nov. 11, 1904, from a field of 10 acres on the Indian Head farm that had never been fertilized. The field was in fallow in 1904 and in 1905 bore a crop of spring wheat, yielding an average per acre of 46 bushels and 54 pounds. The soil from each foot section was removed by means of an auger, carefully sampled, all stones being rejected, and then air-dried. A 5 lb. sample of each foot section was sent by express to the writer. The portion of the soil that passed through a 0.5 mm. sieve was dried at 100° and digested with hydrochloric acid, sp. gr. 1.115, at the temperature of boiling water, for 10 hours.

The percentage of nitrogen seemed so low in comparison with the results of Shutt's analyses that the writer personally took samples from the same field in September, 1905. The nitrogen in this sample from the first foot amounted to 0.25

[1] Report Canad. Expr. Farms, 1897, p. 164.

Table III.—Chemical Analysis of Indian Head Soils.

	First foot.	Second foot.	Third foot.	Fourth foot.	Fifth foot.	Sixth foot.
Insoluble material	74.18	63.42	65.46	70.19	70.03	69.99
K_2O	0.37	0.37	0.41	0.60	0.40	0.42
Na_2O	0.34	0.31	0.37	0.27	0.36	0.28
CaO	1.35	10.12	9.67	7.60	7.02	7.08
MgO	1.45	3.14	3.33	2.97	3.32	3.27
Mn_3O_4	0.07	0.07	0.09	0.06	0.11	0.12
Fe_2O_3	3.94	2.98	2.80	2.79	3.06	3.40
Al_2O_3	6.71	4.30	4.35	3.39	4.02	3.54
P_2O_5	0.17	0.14	0.14	0.17	0.16	0.18
SO_3	0.06	0.03	0.07	0.08	0.43	0.09
CO_2	0.46	9.51	9.93	8.00	7.57	7.13
Volatile matter	10.87	5.52	3.45	3.03	3.78	3.64
Total	99.97	99.91	100.07	99.15	100.26	99.14
Nitrogen	0.23	0.10	0.04	0.04	0.04	0.04
Hygroscopic coefficient	10.7	6.5	6.3	4.3	3.9	5.0

per cent and in that from the second foot to 0.11 per cent, agreeing well with the results of the analysis of the samples taken the previous year. The amount of nitrogen in the surface soil is large, but smaller than that found by Shutt in surface soils from other parts of the same steppe ; it is probable that the latter were sampled to a depth of only 4 or 6 inches. The percentage of potash is high and that of phosphoric acid fairly high, at all depths. The mineral constituents, with the exception of the carbonates, are uniformly distributed. In the presence of the generous supply of calcium carbonate the soil should be considered as of the first quality.

While the chemical analysis indicates this to be a fertile soil, there is nothing in the analytical results to explain the remarkable crop yields that have been obtained. There was, however, found to be something striking in the relation of the moisture content of the fields under different surface conditions. A comparison of the moisture content of the third, fourth, fifth and at times even the sixth foot of a field, that had just brought a crop of cereal or grass to maturity, with that of a field of fallow, even in a year of unusually abundant and well distributed rainfall, indicated that the moisture stored in the subsoil played a very important part in the production of the large yields. Even in the absence of any moisture determinations, the casual examination of the first 4 feet of soil of adjoining fields, that possess a similar surface soil, will show that studies of the soil to a depth of only 16 inches or even, in most places, to a depth of 3 feet are insufficient. The fourth foot of boulder clay subsoil is moist and sticky in the fallow fields while that in grass and in grain fields, when the plants have just reached maturity, resembles an ash-heap. An examination to a depth of less than 3 feet may, at times, fail to reveal any important difference between moisture conditions of grain and fallow fields. Also, examinations made long before or after the maturing of the crop may fail in the same respect. It appears probable that the soil of the whole first 5.5 feet contributes freely of plant food to the growing crops, supplying not only potassium and phosphorus, but also nitrates, under the system of cultivation employed on the Indian Head

farm. The penetration of the roots to the stored moisture, rather than the elevation of the latter, by capillarity, to the roots, is evident from the extreme dryness of the soil as deep as roots were found and the very rapid rise in the moisture content through the succeeding 6 inches, in the case of the field of rye grass, mentioned below. It is a very important matter in arid regions whether the roots penetrate the subsoil to the moisture or whether the latter is elevated to them by the slow action of capillarity. If the latter were the case, practically the only plant food furnished them from below would be nitrogen in the form of nitrates, which had been formed by the nitrification of the humus of the surface soil and had afterwards been carried by seepage below the depth of the plant roots. If the surface soil were deficient in calcium carbonate, while the subsoil was well supplied with it, this compound, also, might be elevated in solution. The chemical composition of the subsoil would then be a matter of little importance so long as the amount of calcium carbonate in the surface soil was sufficient to supply not only the lime required for plant growth and to balance the magnesium content, but also to prevent the soil becoming acid in reaction. On account of the abundance of calcium carbonate in the surface soil of the second steppe the depth to which plants of economic importance send their roots will determine to what depth the chemical composition of the soil should be studied. We should thus have to consider, in the case of the fields at Indian head, the total supply of nitrogen, potash and phosphoric acid within reach of the plant as equivalent to 0.23 per cent, 2.15 per cent and 0.77 per cent, respectively, of the surface foot, when the roots penetrate to a depth of 5 feet. The nitrogen of the soil below the first foot is not included in this total because it is not certain that nitrification occurs to any considerable depth below the first foot.[1] The distribution of plant food throughout the whole depth of soil penetrated by the roots has decided advantages over its accumulation near the surface, especially in the case of a soil that is stored with moisture and that must depend for its supply of water upon a light,

[1] Ladd: N. D. Expr. Sta. Bull. No. 47, p. 69.

uncertain rainfall. In the former case food would be furnished in a more or less regular supply from the beginning of the season of plant growth until the end, or until the moisture of the subsoil had been exhausted.

Moisture Conditions of the Surface Soil and of the Subsoil.

The samples were obtained by the writer in July, 1904, and in September, 1905, a 1.5 inch auger being used for the purpose. A large number of samples would have been desirable, but the difficulty of carrying on the investigations, when the drying of the samples had to be done at a distance of over 1,000 miles from the fields, limited the number of determinations. That the samples shipped to this laboratory were fair specimens of the various fields at the different depths was confirmed by the careful examination on the spot of the soil from similar depths in various parts of the fields. Each sample is the average of the foot section from 2 or more holes in the same field, the soil being weighed as soon as removed and placed in light cotton sacks of known weight and later dried in this laboratory at 100°. All determinations were made in duplicate.

The amount of available or "free" moisture, the total moisture less the hygroscopic moisture per acre-foot, is given in Table IV. In the calculation of the weight of water from the percentage of moisture, the writer has assumed the weight of an acre-foot of dry soil to be 3,348,000 pounds.[1] The weight of an acre-inch of water is about 113 tons.

Fields A, B and C are at Indian Head, on the experimental farm, while F and G are 1 mile south of Moose Jaw and 54 miles west of the first-mentioned fields.

Field A was seeded with Western Rye Grass, a native, in 1901, and had been cut for hay every year since, being mown on July 23, 1904, and July 13, 1905. In the latter year, between the time of haying and that at which the samples were taken, 4.26 inches of rain fell.

Field B, which adjoins A, was in fallow in 1904 and in oats in 1905. The crop was cut September 1st.

[1] Shutt: Rep. Canad. Expr. Farms, 1900, p. 157.

Field C was in fallow in 1904 and in wheat in 1905. The crop was cut on August 27th.

F and G were adjoining fields on the same farm. They were selected because they promised to give the extremes of moisture content on the type of soil of which they were representative. The latter is a very heavy, lacustral clay, uniform to a depth of more than 6 feet. F was an unusually well-tilled summer-fallow, having been in wheat in 1904, while G, which had been fallowed the previous year, bore a very heavy crop of wheat in 1905. It had been cut about September 1st.

In 1904, the last rain previous to the time of sampling was on July 17th, when 0.15 inch fell. In the following year heavy showers fell at Indian Head on August 30th and 31st., amounting to 1.28 inches of rain. At Moose Jaw, in the same year, no rain had fallen during the 10 days preceding the day on which the samples were secured.

The depth to which the chemical composition of the soil needs to be investigated is an unsettled question. That a depth of 1 foot or less is quite insufficient in the case of soils on the second steppe is evident from the above data. About 400 tons of water had been removed from the subsoil of fields B and C from depths of more than 1 foot. In the case of field G probably over 600 tons had been removed from the soil below a depth of 12 inches. These quantities of water, under the climatic conditions there prevailing, must have been removed almost entirely by the transpiration of the wheat and oat plants. According to the experiments of King[1] this weight of water would account for the growth of about 1 ton of dry matter, or approximately 15 bushels of wheat per acre. The ratio of grain to straw on field G was found to be 1.00 to 1.35, both dried at 100°. If such a large amount of water remains in contact with the particles of the deeper portions of the subsoil for nearly a year and does not pass through the surface soil on its way to the plant roots, the food supply of the plants must be largely affected by the chemical composition of the subsoil. Investigations[2] of the moisture content of the soil to

[1] King: "Irritation and Drainage," p. 97 (1899).
[2] Shutt: Rep. of Canad. Expr. Farms, p. 157 (1900).

Table IV.

Available moisture in fallowed fields compared with that in fields that have just brought a cereal or grass crop to maturity. The water is expressed as tons per acre-foot.

Field.	Date.	First foot.	Second foot.	Third foot.	Fourth foot.	Fifth foot.	Sixth foot.	Total.
A	July 25, 1904	127	75	97	112	84	101	596
"	Sept. 4, 1905	268	157	167	177	170	152	1091
	Excess in second year	141	82	70	65	86	51	495
B	July 25, 1904	291	184	196	199	236	194	1800
"	Sept. 5, 1905	179	95	77	69	167	211	798
	Excess in fallow	112	89	119	130	69	—17	502
C	July 25, 1904	350	272	279	216	144	. .	1261
"	Sept. 5, 1905	270	158	144	97	182	. .	734
	Excess in fallow	80	114	135	119	—38	. .	527
F	Sept. 9, 1905	162	412	360	266	236	231	1667
G	"	144	99	104	194	213	228	982
	Excess in fallow	18	313	256	72	23	3	685

a depth of 16 inches have failed to account for the good yields of grain obtained from the fallowed fields in dry seasons, while the explanation becomes evident when the investigations are carried to a depth of 6 feet. It is probable that the chemical as well as the physical properties of the subsoil play an important part in the production of cereal and grass crops on the great plains.

Ten Eyck[1] has found that the roots of wheat, oats and various grasses reach a depth of from 4 to 6 feet in North Dakota and in Kansas. Evidently the great depth of root penetration is characteristic of the whole of the great plains region.

Summary and Conclusions.

In the following there are given some conclusions of a purely agricultural nature. The detailed discussion of the data upon which they are based will be published elsewhere, in the near future.

1. The region of prairie and plain north of the northern boundary of the United States consists of 3 prairie levels or steppes.

2. The remarkably large crop yields obtained on the second steppe are confined to wheat, oats, barley, peas and potatoes.

3. These high yields have, in general, been obtained from fields that were, during the previous season, under clean cultivation, summer-fallow, or were in cultivated crops, as corn and potatoes.

4. The moisture stored in the subsoil during the previous summer and not the frost of the preceding winter, is the cause of the high yields.

5. The soil of the southern portion of the second steppe does not remain permanently frozen at any depth.

6. The surface soils are rich in nitrogen and both surface soil and subsoil are well supplied with potash and phosphoric acid. The subsoil is very rich in carbonates.

7. The roots of cereals and grasses penetrate the subsoil to

[1] Bulls. 36 and 43, N. D. Expr. Sta.; No. 127 Kansas Expr. Sta.

depths of from 5–6 feet, even in seasons of unusually heavy and well distributed rainfall.

8. The total yield of dry matter of wheat, oats and barley varies as the rainfall of the crop season, but shows a still closer relation to the total available moisture of the crop season.

9. In the case of wheat the yield of grain from fallowed fields is largely independent of the rainfall of July and August, provided that the rainfall of May and June has been abundant.

10. Investigations of the fertility of the soils of the second steppe, in which only the first 16–36 inches are considered, do not furnish sufficient data upon which to base generalizations; in all such investigations the composition of the soil to a depth of 5 or 6 feet should be considered.

11. The relative fertility of different areas seems to depend upon the nature of the subsoil rather than upon that of the surface soil, the latter, in general, being rich enough to produce very heavy crops when the moisture conditions are favorable.

UNIVERSITY PLACE,
NEBRASKA.

IONIC VELOCITY AND IONIC HYDRATION.

[FIRST COMMUNICATION.]

BY CHARLES G. CARROLL.

That there is a relation between ionic friction and the mechanical friction, or viscosity of the solvent, has long been held. To account for this relation Kohlrausch[1] proposes the following hypotheses: "About every ion moves an atmosphere of the solvent whose dimensions are determined by the individual characteristics of the ion . . . The electrolytic resistance of an ion is a frictional resistance that increases with the dimensions of the atmosphere . . ." Into this form Kohlrausch puts the commonly held conception of ionic hydration or combination of ion and solvent. Numerous attempts have been made to measure the amount of such hydration, and an

[1] P. Roy. Soc., 71, 338.

actual transport of solvent with the ions has been demonstrated by Morgan and Kanolt[1] and by Buchböck.[2]

The evidence for the Kohlrausch hypothesis was, however, incomplete and no attempt was made to put it on a quantitative basis. A quantitative application was made by the writer,[3] in the case of certain ions and salts, in methyl and ethyl alcohols as solvents. It was shown that, for a considerable range of temperature, the maximum molecular conductivity of any given salt varies inversely as the coefficient of viscosity, or,

$$\mu_\infty \eta = \text{constant.}$$

In every case considered, embracing all the data available at the time, good agreement between fact and theory was found, and recently Walden[4] has shown that the foregoing relationship holds for tetraethylammonium iodide in some 20 organic solvents.

No general law has been found to hold for ionic velocities, or conductivities, in aqueous solution. The purpose of the present paper is to show that a general law relating to ionic velocity, or conductivity, viscosity and other properties of solvent and solute exists for solutions in water and methyl alcohol. This law may be stated as follows:

The velocity of a given ion, under a constant fall of potential, is directly proportional to the valence of the ion, the cube root of the ionic (atomic) volume, the specific inductive capacity, or dielectric constant, of the solvent, and is inversely proportional to the viscosity coefficient of the solvent.

Formulated, the law is, for cations,

$$\frac{c\,\eta}{n_1\,D.V_c^{1/3}} = K_c;$$

for anions,

$$\frac{a\,\eta}{n_2\,D.V_a^{1/3}} = K_a,$$

[1] THIS JOURNAL, 28, 572.

[2] Z. physik. Chem., 48, 563.

[3] Dissertation, Johns Hopkins University, 1904. Jones and Carroll: THIS JOURNAL, 32, 521.

[4] Z. physik. Chem., 55, 207.

where c and a are the velocities of cation and anion, respectively, n_1 and n_2 their valences, η is the viscosity coefficient; D, the dielectric constant of the solvent; and $V_c^{1/3}$ and $V_a^{1/3}$ are the cube roots of the atomic volumes of the elements yielding the ions. It is assumed that, for the same element, ionic and atomic volume are equal. Accordingly, if the ions be spherical in shape, the cube roots of the various atomic volumes will be proportional to the various atomic, or ionic, radii.

The law may be tested by the use of relative ionic velocities, or by the use of conductivity data, if the values of the constants K_c and K_a have been determined, for we have

$$\frac{(c+a)\eta}{D\left(n_1 V_c^{1/3} + \frac{K_a}{K_c}.n_1.V_a^{1/3}\right)} = \text{constant.}$$

In this case n_1 and n_2 are the number of unit changes carried by cation or anion, or cations or anions, collectively.

In the following table are given the results of a comparison for certain ions in aqueous and methyl alcoholic solution.

Table I.—Values of K_c and K_a for Various Ions.

$\eta_{H_2O} - 18° = 0.01054$.[1] $\eta_{CH_3OH} - 25° = 0.00553$.[1]

$D_{H_2O} - 18° = 80.8$.[2] $D_{CH_3OH} - 25° = 31.7$.[3]

Ion.	Ionic volume.[3]	Velocity, H_2O.[4]	Velocity, CH_3OH.[5]	$K_{c,a} \times 10^5$, H_2O.	$K_{c,a} \times 10^5$, CH_3OH.
Li	11.9	33.4	27.8	191	212
Na	23.7	43.6	37.3	198	227
K	45.5	64.7	45.9	236	224
Rb	56.3	68.0		231	
Cs	70.6	68.0		215	
Ca	25.3	51.8		230	
Sr	34.5	51.7		207	
Ba	36.5	55.5		218	
Cl	25.4	65.4	49.5	290	294
Br	25.6	67.6	50.2	299	297
I	25.6	66.4	52.4	293	310

[1] Thorpe and Rodger: Phil. Trans., 185A, 397.
[2] Drude: Wied. Ann., 59, 49.
[3] Ostwald: "Lehrbuch," I., 854.
[4] Kohlrausch: Sitzun. d. k. p. akad., 26, 572.
[5] Carrara: Gazz. chim. ital., 26, 179.

The mean value of K_c is 220, of K_a 297. The ratio K_a/K_c equals 1.35. With certain exceptions the values for the constants agree tolerably well, particularly in the case of the ions in methyl alcohol.

It remains to test the law by means of conductivity data. This is done in the following tables:

Table II.—Values of K for Various Salts in Aqueous Solution.

$K \times 10^5$.

	Cl.	Br.	I.	NO_3.	SO_4.
Li	208			200	
Na	209	219	216	201	204
K	226	230	228	215	224
Rb	222				
Cs	216				
Ca	219			205	218
Sr	217			202	
Ba	216			191	
Zn	236				229
Mg	226				205
Tl	237	237		224	
Cd	220				213

For RbCl, $CaCl_2$, $BaCl_2$, $SrCl_2$, $ZnCl_2$ and $MgCl_2$ the value of $\mu_{10,000}$ was used, for TlCl μ_{2048}, and for $CdCl_2$ μ_{2000}. In the other cases μ_∞ was used. The values for certain nitrates and sulphates are given. These were calculated, using Kopp's[1] values for the volumes of the NO_3 and SO_4 groups. The conductivity data were taken from Landolt and Börnstein's "Tabellen," ed. 1905. The values for the constants, D, η, etc., are from the same sources as in Table I.

Table III.—Values of K for Various Salts in Methyl Alcohol Solutions.

		$K \times 10^5$.
NaCl	25°	227
NaBr	25°	233
NaI	18°	230
KCl	25°	227
KBr	25°	229
KI	18°	217

[1] Ostwald: "Lehrbuch," I., 845.

The values for μ_∞ at 25° were taken from the results of Carrara ;[1] those at 18° from Völlmer.[2] Values of other constants were obtained from sources already indicated.

Finally, it can be shown that the foregoing law is susceptible of a simple physical explanation.

Assuming the ion to be spherical in shape and that the charge carried is uniformly distributed over its surface, as is the case with a charged spherical conductor, the capacity of the ion, considered as a spherical condenser, will be found from the relation,

$$\pi = e/c, \tag{1}$$

where π = potential, e = quantity and c = capacity. The capacity of a sphere varies directly as its radius ;

$$c = \text{K. V, or, for the ion}$$
$$c = \text{K. } V^{1/3} \text{ and}$$
$$\pi = \text{K. } e/V^{1/3}. \tag{2}$$

Now, if a charged body is brought into the presence of particles of substance free to move, these, if of greater specific inductive capacity than the surrounding medium, will be attracted to the charged body, thus running down the energy of the field around the charged body. It is reasonable to suppose that in different cases the amount of such lowering of energy is equal. Applying these considerations to the ions, the thickness of the shell of solvent formed at any point by attraction, will be determined by the potential at that point and by the specific inductive capacity of the solvent,

$$r_s = \text{K.} \frac{\pi}{D} = \text{K.} \frac{1}{D.V^{1/3}}, \tag{3}$$

since

$$\pi = \text{K.} \frac{1}{V^{1/3}}.$$

According to Stokes, when a sphere moves with a small velocity in a viscous fluid, the frictional resistance is proportional to the product $\eta\, r\, V$, V being the velocity, r the radius of the sphere and η the viscosity coefficient, and the limiting

[1] *Loc. cit.*
[2] Wied. Ann., 53, 328.

velocity of the sphere, when the force acting is uniform, is inversely proportional to the product $r\,\eta$.

Applying this to the ion and its shell of solvent and taking the thickness of the shell, r_s, as equal to the effective ionic radius, or actual ionic radius plus shell thickness, we have, for ionic velocity,

$$V = K.\ \frac{1}{\eta\, r_s}, \tag{4}$$

and substituting for r_s its value from (3), we get

$$V = K.\ \frac{D\, V^{1/3}}{\eta}, \tag{5}$$

which is a different form of the original equation formulating the law.

In the foregoing derivation it is assumed that the thickness of the shell of solvent, r_s, is so great as compared with the real ionic radius, $K.\ V^{1/3}$, that r_s may be put for $r_s + K.\ V^{1/3}$ without much error. It is evident that for ions of large ionic volume r_s and $K.\ V^{1/3}$ must be more nearly equal than for ions of small ionic (atomic) volume. The complete expression would be

$$V = K_1\ \frac{1}{\eta\left(K_2\, V^{1/3} + K_3.\ \frac{1}{D.V^{1/3}}\right)}.$$

If $K_2V^{1/3}$ is small as compared with $K_3.\frac{1}{D.V^{1/3}}$, we get equation (5). Here, then, we have a possible explanation of some of the discrepancies in Table I.

Summary.

1. The hypothesis of ionic hydration has been shown to be capable of a quantitative application in the form of a general conductivity law.

2. This law has been shown to have a simple physical explanation.

CHEMICAL LABORATORY,
UNIVERSITY OF ARKANSAS,
July, 1906.

Contributions from the Chemical Laboratory of Harvard College.

1,3,5-TRIIOD-2-CHLORBENZENE.

By W. V. Green.

Much work has been done in this laboratory on the replacement by hydrogen of bromine or iodine attached to the benzene ring, under the influence of sodic ethylate, sodic malonic ester, or sodic acetacetic ester. In most cases the halogen replaced by hydrogen has stood in the diortho position to 2 nitro groups, but it has been found also[1] that this reaction takes place, when the atom of halogen is in the diortho position to 2 atoms of bromine or chlorine. The work described in this paper was undertaken with the intention of studying the effect of 2 atoms of iodine on an atom of halogen standing between them, but unexpected obstacles have delayed it so much that only one preliminary experiment of this sort could be tried; nevertheless, as I shall be unable to continue the work in this laboratory next year, it seems best to publish this description of the results obtained.

The 1,3,5-triiod-2-chlorbenzene was made by replacing with chlorine the amino group in symmetrical triiodaniline, but if the triiodaniline was not carefully purified, another substance was formed, which it was found impossible to separate from the desired product. The triiodchlorbenzene melts at 119°–120°, and, when boiled for 6 hours with an alcoholic solution of sodic ethylate, gave up iodine, although the reaction was far from complete. Only a single experiment was tried with a small amount of material, so that more work is necessary to understand the nature of the reaction, but there seems no doubt that this compound behaves differently from the corresponding tribromchlorbenzene, which is unaffected by sodic ethylate under these conditions. The subject, therefore, deserves further study, which will be given to it in this laboratory.

When treated with cold, fuming nitric acid the triiodchlorbenzene is converted into triiodchlordinitrobenzene, which de-

[1] Jackson and Calvert: This Journal, 18, 298. Jackson and Gazzolo: *Ibid.*, 22, 50.

composes and melts from 266°–269°. This seems to be a very reactive substance, as preliminary experiments showed that it acted with aniline, sodic ethylate, sodic malonic ester, or sodic acetacetic ester. These reactions will also be studied in this laboratory.

Preparation of 1,3,5-triiod-2-chlorbenzene, $C_6H_1I_3Cl$.—The triiodaniline was prepared by a process founded on those of Michael and Norton[1] and of Jackson and Langmaid,[2] as follows: Ten grams of freshly distilled aniline, dissolved in 500 cc. of strong hydrochloric acid and diluted up to 7 liters, were treated with 54 grams of the monochloride of iodine, ICl, introduced by passing a stream of air through the flask containing the chloride, which was heated to 60°. The introduction of the chloride took from 90–110 minutes. The brown precipitate formed at first and the straw-yellow one deposited later, are both triiodaniline, and the yield of this crude product in the most favorable cases ran as high as 90 per cent of the theory. The triiodaniline thus obtained was recrystallized from chloroform until it showed the melting point 184°–185°. If the crude product was used in making the triiodchlorbenzene, a substance melting at 166° was also formed, which it was almost impossible to separate from the desired product. This impurity seemed to be due to the use of an excess of chloride of iodine in making the triiodaniline; and, as in this case, vapors of iodine were given off during the diazo reaction, giving $C_6H_1I_3Cl$, it is possible that these phenomena may be due to the introduction of iodine into the amino group. The filtrate from the triiodaniline should not be used for dissolving a fresh portion of aniline for a second operation, as this gave a much less pure product than when fresh hydrochloric acid was used.

The triiodaniline was converted into triiodchlorbenzene as follows: Ten grams of the triiodaniline were treated with 120 cc. of strong hydrochloric acid and 15–20 grams of very finely powdered sodic nitrite added to it in small portions at a time; after each addition the mixture was shaken in a loosely corked

[1] Ber. d. chem. Ges., **21**, 1707 (1888).
[2] THIS JOURNAL, **32**, 300 (1904).

flask, until all red fumes had been absorbed. The decomposition of the diazo compound was then brought about by heat and the flask allowed to stand on the steam-bath for 2 hours after the evolution of nitrogen had slackened. The product was purified by washing with sodic hydrate and water, followed by crystallization from a mixture of benzene and alcohol, until it showed the constant melting point 119°–120°, when it was dried at 100° for analysis. If the product was very tarry, it was found advisable to wash it with ligroin and later with small quantities of ether and with alcohol, before crystallizing. Treatment with bone-black absorbed much of the substance and sublimation gave unsatisfactory results. The yield varied from 80 to 85 per cent of the thory.

I. 0.1926 gram substance gave 0.3312 gram AgI + AgCl.
II. 0.1402 gram substance gave 0.2413 gram AgI + AgCl.

	Calculated for $C_6H_2I_3Cl$.	Found. I.	II.
I + Cl	84.92	84.37	84.47

Properties of Triiodchlorbenzene (1,3,5,2).—When crystallized from a mixture of benzene and alcohol it forms slender prisms, terminated by pyramids, which are probably white, but could not be obtained free from a faint pinkish tinge. These appear, when seen with the naked eye, as thick masses of branching needles. It melts at 119°–120°, and is freely soluble in ether, chloroform, acetone, benzene, toluene, carbonic disulphide, or ethyl acetate; somewhat soluble in glacial acetic acid or acetic anhydride; very slightly soluble in cold alcohol, or methyl alcohol, more soluble in them when hot; essentially insoluble in ligroin, water, or cold amyl alcohol, moderately soluble in hot amyl alcohol. Aniline dissolves it freely, forming a red solution, but no halogen is removed. The best solvent for it is a mixture of benzene and alcohol. It does not seem to be affected by the 3 strong mineral acids, or sodic hydrate, but fuming nitric acid acts upon it in a way described later in this paper.

A preliminary experiment was tried on the action of sodic ethylate with the 1,3,5-triiod-2-chlorbenzene. The alcoholic solution used contained more than enough ethylate to remove

all the halogen and it was mixed with enough anhydrous benzene to insure the solution of the triiodchlorbenzene. The mixture, which took on a pinkish color at once, was heated on the steam-bath, under a return condenser, for 6 hours, when it passed through red to brownish-red. It was poured into a quantity of water, which formed a viscous, red precipitate and yellow, turbid liquid, and the mixture was allowed to stand for 2 days to get rid of the benzene before it was filtered. Unfortunately, the amount of material available for this experiment, a little over 0.8 gram, was so small that no investigation was possible of the red organic product, which had a characteristic smell like apples. The still turbid, aqueous filtrate was acidified with nitric acid and filtered again from a slight precipitate; on acidification the color of the liquid changed from yellow to red, probably from the formation of some free iodine, which was detected by starch paste and by carbonic disulphide. This filtrate, which became colorless on standing over night in a stoppered flask, was made up to 1 liter, and 2 measured portions were treated with argentic nitrate, which gave a yellowish-white precipitate. There can be no doubt from these results that sodic iodide was one of the products of the reaction, but the amount of AgI obtained was less than 30 per cent of that which would have been formed, if 1 atom of iodine had been removed. It is evident, therefore, that the reaction was far from complete. This replacement of iodine shows that the behavior of the triiodchlorbenzene with sodic ethylate is different from that of the corresponding tribromchlorbenzene, which is unaffected by sodic ethylate under these conditions. An attempt was next made to determine whether this precipitate contained AgCl as well as AgI. With this intention it was washed with ammonic hydrate, which removed only about the amount of silver salt corresponding to the solubility of AgI in ammonic hydrate; it is probable, therefore, that no AgCl was present, but further experiments are necessary to decide the question.

1,3,5-Triiod-2-chlordinitrobenzene, $C_6I_3Cl(NO_2)_2$.—The triiodchlorbenzene was dissolved in cold, fuming nitric acid, when, after standing for a short time, long needles of the

dinitro compound separated. The mixture was then diluted with water, warmed on the steam-bath, filtered and washed. The filtrate gave no test for a halogen. The organic product was recrystallized from a mixture of benzene and ligroin until it showed the decomposition point 266°–269°, when it was dried, at 120°, for analysis.

I. 0.1306 gram substance gave 0.1901 gram AgI + AgCl.
II. 0.1341 gram substance gave 0.1949 gram AgI + AgCl.

	Calculated for $C_6I_3Cl(NO_2)_2$.	Found. I.	II.
I + Cl	71.74	71.47	71.34

Properties of 1,3,5-Triiod-2-chlordinitrobenzene.—It crystallizes from a mixture of benzene and ligroin in yellowish-white needles, which, under the microscope, are seen to be prisms terminated by pyramids, or occasionally by a plane at right angles to the axis, which seem to belong to the orthorhombic system. At 266° it turns black, and begins to melt at 267°, but the fusion is not complete until the temperature reaches 269°. It is freely soluble in ether, chloroform, acetone, benzene, toluene, carbonic disulphide, or ethyl acetate; somewhat soluble in glacial acetic acid or acetic anhydride; nearly insoluble in cold methyl, ethyl, or isoamyl alcohol, moderately soluble in these solvents when hot; essentially insoluble in water or ligroin. The best solvent for it is a mixture of benzene and ligroin. The 3 strong mineral acids seem to have no action on it. Sodic hydrate seems to react with it, as a slight precipitate was formed by argentic nitrate in the acidified solution.

The triiodchlordinitrobenzene is a decidedly reactive substance. Aniline forms with it a red solution with the removal of some halogen, when heated on the steam-bath. Sodic malonic ester gives with it a strong red color, sodic acetacetic ester a yellow, sodic ethylate a light red color. In each case a precipitate was formed, when argentic nitrate was added to the acidified solution.

The research will be continued in this laboratory.

CAMBRIDGE, MASS.,
July 9, 1906.

THE NITRATION OF ANILINE AND CERTAIN OF ITS DERIVATIVES. I.

By J. Bishop Tingle and F. C. Blanck.

It is well known that aniline cannot be directly nitrated; under any of the ordinary conditions in which such action might be expected to take place, nitric acid converts aniline into a resinous, tarry, or charred mass. This behavior is usually accounted for by stating that the nitric acid attacks the amino group more readily than the benzene nucleus.[1] A little thought will show that such a statement, although it *may* be true, is really devoid of any experimental foundation and that certain rather serious objections could be urged against it. For instance, it has been suggested by some chemists that substitution in the nucleus is really preceded by substitution in the side chain and subsequent rearrangement. Further, the amino group is even more sensitive towards nitrous acid than towards nitric acid, as is shown by the fact that, in general, nitrites of the aromatic amines cannot be prepared, whereas the nitrates are usually stable; moreover, in carrying out the diazo reaction, some tarry matter is always formed and unless considerable care is taken to adjust the conditions of the experiment specially for each individual amine, this tar is apt to be the chief, or even the only tangible product of the reaction.

Guided by these considerations, we decided to reinvestigate the direct nitration of aniline and to begin a systematic survey of the influence, on nitration, of the substitution in aniline of one or both of the hydrogen atoms of the amino group. Coupled with this, however, is the further question of the influence exercised on the substitution by admixture of the nitric acid with other acids. These points are illustrated by the fact that dimethylaniline yields the paranitro derivative when nitrated in the presence of acetic acid,[2] whereas the meta compound is formed if sulphuric and nitric acids be used.[3] A number of cases are on

[1] *Vide*, for example, Lassar-Cohn's "Application of Some General Organic Reactions," translated by J. Bishop Tingle, p. 3, *et seq.*

[2] Ber. d. chem. Ges., **10**, 761.

[3] *Ibid.*, **19**, 198.

record where mixtures of nitric and acetic acids *or* nitric and sulphuric acids have been employed to nitrate some compound, but this is the only example which we have been able to find in the literature of nitration experiments having been made on a given aniline derivative with each of these mixtures of acids. The influence of the substituting group is shown by the fact that formanilide, for example, yields the paranitro derivative by direct nitration,[1] whereas, under the same conditions, acetanilide gives rise to a mixture of ortho and paranitro compounds.[2]

The investigation just outlined will, naturally, extend over a considerable time and we wish to reserve the field by the publication of this paper, which, although it is of a preliminary nature, contains results that we think may prove to be of some general interest.

Nitration of Aniline.—Our experiments in this connection being based upon the hypothesis that nitrous acid might probably be the active agent in producing the decomposition of the aniline, we took every precaution in our power to exclude this substance and to remove it if it were formed. Accordingly, the nitric acid which was used was freed from dissolved oxides by means of a current of dry air and, as far as possible, oxidation during the experiment was avoided by employing nitric acid of 99 per cent concentration and freshly distilled aniline. We carried out the experiments in platinum vessels, placed in a freezing mixture, so as to keep the temperature as low as possible, and took care that the reagents were gradually mixed and thoroughly stirred; moreover, we operated in the presence of urea, in the hope that any nitrous acid which might be produced by the possible reduction of some of the nitric acid would be instantly decomposed by this reagent. In the later experiments we employed aniline nitrate in place of aniline, so as to eliminate the heat of formation of this salt. In every experiment, however, it was found to be impossible to keep the temperature sufficiently low and, as soon as it rose, tarry, or carbonaceous products were formed. The

[1] THIS JOURNAL, 8, 346.
[2] "Jahresb.," 1875, p. 344. THIS JOURNAL, 11, 320.

result was identical whether the acid was added to the aniline or *vice versa*.

These experiments were, therefore, discontinued and another series undertaken in order to determine at what concentration of nitric acid the formation of aniline nitrate ceases and nitration—or charring—begins. The results demonstrated that any strength of acid could be used up to at least 75.33 per cent HNO_3, provided, in the case of the more concentrated acids, above 50 per cent, that the mixture was cooled and excess of acid was avoided. Acids of 50.71–75.33 per cent always gave, with aniline, a pink-colored solid, which was stable at 0°; the color was at once discharged by the addition of a little water, or of a few drops of aniline. Slight excess of acid increased or restored the color, as the case might be, but if this additional acid was of sufficient concentration then, sooner or later, depending on this concentration and on the temperature, the pink color darkened, finally becoming black and the whole mass gradually charred, sometimes becoming incandescent. We have been unable to find any previous record of these phenomena.

With acid above 75.33 per cent HNO_3, charring took place rather quickly although the aniline was in considerable excess. We believe, however, that this was due to the impossibility of preventing local superheating, *i. e.*, to the action of the concentrated acid, at a relatively high temperature, on aniline nitrate. Be this as it may, it is certain that with acids containing up to 75.33 per cent HNO_3, any charring which may be brought about is due to an attack on aniline nitrate and not to one on free aniline. We emphasize this rather obvious fact in order to contrast it with the behavior of aniline towards a mixture of nitric and sulphuric acids, in which the latter is in considerable excess. In these circumstances, as is well known, nitration proceeds smoothly, because, as it is usually expressed, the sulphuric acid "protects" the amino group. Surely, however, the amino group is equally well "protected" in the nitrate,

$$C_6H_5NH_2NO_3,$$

as in the sulphate,

$C_6H_5NH_2SO_4H$,

and the excess of concentrated sulphuric acid which is present must abstract so much water from the nitric acid as to make it of a higher concentration than 75.33 per cent HNO_3. The only very obvious difference in the conditions of the 2 experiments, so far as we can see, is in that which governs the temperature. In the experiment with sulphuric acid all the materials are in solution and the "heat of nitration," as it may be termed, is instantaneously absorbed and diffused throughout the large volume of comparatively indifferent sulphuric acid, whereas, in our experiments with aniline nitrate and nitric acid, we had to rely on the relatively slow, inefficient and clumsy mechanical means of stirring and external cooling to neutralize this heat. We hope, later, to recur to this point, when more experimental data have been accumulated.

Nitration of Anilines Substituted in the Amino Group.—A considerable amount of scattered work, which will be cited in due course, has been done on the nitration of compounds of the types C_6H_5NHR, C_6H_5NRR' and $C_6H_5N:R''$, and in some of these experiments the nitric acid was mixed with sulphuric or acetic acids. This portion of our investigation has been carried out with the following reagents: 1. Nitric acid, sp. gr. = 1.46,[1] containing 80 per cent HNO_3; 2. Nitric acid, sp. gr. 1.46, with glacial acetic acid, usually in the proportion 1.25 mols. of nitric acid : 4 mols. of acetic acid, or 1.25 mols. of nitric acid : 8 mols. of acetic acid; 3. Nitric acid, sp. gr. = 1.46, and anhydrous oxalic acid, in the proportion 1.25 mols. of nitric acid : 4 mols. of oxalic acid; 4. Nitric acid, sp. = 1.46, and trichloracetic acid, in the proportion 1.25 mols. of nitric acid : 4 mols. of trichloracetic acid; 5. Nitric acid, sp. gr. = 1.46, and concentrated sulphuric acid, sp. gr. = 1.83, containing about 92 per cent H_2SO_4, in the proportion of 1.25 mols. nitric acid : 4 mols. of sulphuric acid. The dissociation constants of these admixed acids are as follows: Acetic acid, $K = 0.0018$; oxalic acid, $K = 10.00$; trichloracetic acid, $K = 121.00$; sulphuric acid, $K = 130.0$, approximately, by calculation. It will be observed that we have selected, for admixture with the

[1] Remsen and Graham: THIS JOURNAL, 11, 320.

nitric acid, acids of widely differing strength. Acetic is a typical "weak" acid; trichloracetic is, practically, the strongest organic acid which is known and certainly the strongest which is available for use in any quantity. Oxalic acid was selected partly because it is dibasic, but chiefly because of its intermediate position between the other two. The use of sulphuric acid was dictated by the fact that it is the only "strong" inorganic acid suited for the purpose in view. It will be noticed that, in so far as "strength" is concerned, sulphuric and trichloracetic acids are in the same class[1] and should, therefore, permit of a conclusion being drawn as to the influence, if any, of the mono or dibasicity of the admixed acid and of its organic or inorganic composition, *i. e.*, as to the possible specific influence of a carboxyl group.

As far as possible, we desired to avoid the formation of di- or polynitro derivatives, consequently, our experiments were usually carried out at room temperature; in cases where there was a considerable evolution of heat on mixing the substances, cooling with ice-water was resorted to. Sometimes the mixtures were surrounded by crushed ice during the whole time of an experiment and occasionally gentle warming was requisite to promote a reaction.

Formanilide.—This substance yields paranitroformanilide by direct nitration.[2] In the presence of sulphuric acid we have obtained the *meta derivative.*

Acetanilide.—This compound, by direct nitration, gives a mixture of ortho and para derivatives.[3] In the presence of acetic acid no nitration took place under the conditions of our experiments. With oxalic acid we obtained *paranitroacetanilide* in good yield. The same result was produced by the use of trichloracetic acid, which was ground up with the acetanilide and the mixture added to the nitric acid. Sulphuric acid yielded *metanitroacetanilide.* This last result differs from the experience of Nöltingand Collin,[4] who, however, operated in a freezing mixture of ice and salt and, nitrating in the presence of

[1] Cf. Kastle: THIS JOURNAL, 33, 52 (1905).
[2] *Ibid.*, 8, 346.
[3] "Jahres.," 1875, p. 344. THIS JOURNAL, 11, 320.
[4] Ber. d. chem. Ges., 17, 261.

both acetic and sulphuric acids, obtained the para and ortho derivatives.

Benzoylanilide.—A mixture of ortho, meta and paranitro derivatives is formed by the direct nitration of this compound.[1] Operating in the presence of sulphuric acid we have only found the *para compound.*

By the use of acetic acid we have obtained the *meta isomer*, practically without admixture.

Methylaniline.—Our experiments with this substance, in the presence of acetic acid, failed to yield any positive result. Sulphuric acid causes the production of the metanitro derivative.[2]

Ethylaniline.—This body behaved, with acetic acid, like the methyl compound. In the presence of sulphuric acid meta and para derivatives are formed.[3]

Dimethylaniline.—For the sake of completeness we include this substance, although we have no results of our own to communicate at present. Acetic acid is stated to produce the paranitro derivative,[4] whereas sulphuric acid gives rise to the meta compound.[5]

Diethylaniline.—In our experiments with this substance, in the presence of acetic acid, nitration failed to take place. Sulphuric acid has been found to produce chiefly the meta derivative, together with some para compound.[6]

We think that our results justify the statement that *the position assumed by the entrant nitro group is definitely influenced both by the acid present with the nitric acid and also by the N-substituents.*

We hope to give full details of our experiments later, when the work on the subject, which is now in progress in this laboratory, is more nearly complete.

JOHNS HOPKINS UNIVERSITY,
June, 1906.

[1] Ann. Chem. (Liebig), 208, 292.
[2] Centrabl., 1901, I., p. 105.
[3] Ber. d. chem. Ges., 19, 546.
[4] *Ibid.*, 10, 761.
[5] *Ibid.*, 19, 198.
[6] *Ibid.*, 19, 199.

ON A NEW METHOD FOR THE PREPARATION OF STANDARD SOLUTIONS.

By S. F. Acree and R. F. Brunel.

At the time of the publication of some work which appeared with the above title[1] the writers had overlooked the work of G. T. Moody[2] on the use of this method for the preparation of standard solutions of hydrochloric acid. The work is being continued as announced.

Johns Hopkins University,
Nov. 1, 1906.

OBITUARY.

FEDOR F. BEILSTEIN.

Professor F. F. Beilstein was born in St. Petersburg, February 5, 1838, and died in the same city, October 19, 1906. His chemical education was received from Bunsen, at Heidelberg, and from Liebig, at Munich, and he obtained the Ph.D. degree from the University of Göttingen. In 1859, Beilstein was appointed assistant professor of chemistry at the University of Breslau, and in 1866 was called to the chair of chemistry at the St. Petersburg Technological Institute; this appointment he retained until his death. Beilstein's investigations were numerous and some of them had important technological results. They dealt chiefly with compounds of the aromatic series, with the composition of Caucasian naphtha and coal-tar and with analytical methods. His first paper, on the diffusion of liquids, appeared in his eighteenth year.

Professor Beilstein was the author of numerous books, all issued in the German language. By far the most important of these was, of course, his "Handbuch der organischen Chemie" by the publication of which he placed his fellow organic chemists under an immense debt of gratitude. It would, indeed, be difficult to overestimate the enormous influence, direct and indirect, exerted on the progress of organic chemical investigation by this work. Three editions of the "Handbuch" were prepared by Beilstein himself. Later, he transferred his rights to the German Chemical Society which has issued the supplementary volumes. Beilstein was elected a member of the St.

[1] This Journal, 36, 117.
[2] J. Chem. Soc., 73, 658.

Petersburg Academy of Sciences in 1886, an "Honorary Member" of the German Chemical Society in 1894, and a "Foreign Member" of the London Chemical Society in 1883.

REPORT.

The Interaction of Chlorine and Hydrogen.

In a recent article[1] C. H. Burgess and D. L. Chapman describe the results obtained from a number of experiments carried out to determine the cause of the so-called "induction period," or period of comparative inactivity in the initial union of chlorine and hydrogen. The hypotheses advanced by numerous investigators of this phenomena can be grouped under one of three heads:

(*a*) The action is due to the power which light has of increasing the electro-negative properties of chlorine.

(*b*) The cause of the resistance to the action is in some manner removed by the action of light.

(*c*) The action is due to the formation and interaction of intermediate products. All theories were studied and found to afford unsatisfactory explanations of the phenomena.

Van't Hoff has suggested that as an induction period is not characteristic of a simple chemical reaction, the phenomena in question was due to the omission of some necessary experimental precaution. Experiments to test this point soon showed that the action is due to the presence of impurities which would produce the results noticed and would account for many of the observed facts. The mixture of chlorine and hydrogen employed was obtained by the electrolysis of a strong aqueous solution of hydrogen chloride. The actinometer in which the experiments were carried out was placed in a tank of water to keep the temperature constant.

When the apparatus is filled with the electrolytic gas and ordinary tap water and exposed to light there is no effect for some time; finally, however, the action begins and gradually increases in speed to a maximum, then falls slightly and eventually becomes constant. After this stage has been reached the gases can again be rendered inactive by shaking the vessel in which they are contained. This can be repeated a number of times, the induction period, however, becoming shorter each time. Even when the greatest precautions are taken to render the gas active, the inactivity is restored by allowing the gas to stand in the dark. If the chlorine is separately rendered active

[1] J. Chem. Soc., 89, 1399 (1906).

it has no more effect upon the result than if the action takes place in the presence of the hydrogen. The facts all seemed to point to the conclusion that there was some principle which caused a resistance to combustion and which could be destroyed by light. It was present in ordinary water and freshly prepared chlorine, but not in hydrogen. At first it was thought that the restoration of this property when the gases were allowed to stand in the dark, would shut out all possibility of the action being due to any material substances.

Solutions of salts and acids were found to have a more marked influence upon the induction period than water alone; but this action can be decreased or prevented by keeping the vessel at the boiling-point of water for some time. It was found possible to prepare crystals of barium chloride, which had lost the property of destroying or removing the activity of electrolytic gas; such material is termed "active;" when these crystals were left for some time between folds of filter paper they became "inactive." It was also found that active solutions could be prepared, some of which contained no free chlorine and others were produced entirely without the agency of this element; the presence of oxygen had no influence on the action.

The evidence pointed to the fact that the substance which produced the induction period was present in the mixture used, or was extracted from the air.

Small amounts of ammonia were found to cause the induction period and to form with chlorine a product which is volatile at ordinary temperatures and can be removed from solution by exhaustion.

In these particulars there was an agreement between the results observed in the ordinary manner and those produced artificially, by the addition of the substances in question. If the impurities are completely removed and all outside contamination is prevented, there is no decay of the activity. When small quantities of ammonia were added, the induction period was roughly proportional to its amount. Other substances such as alcohol, ether, sulphur dioxide, hydrogen sulphide, nitrous or nitric acids, stannous chloride, hydrogen peroxide, potassium permanganate, etc., caused no decrease of activity. That the inactivity was restored when the gas, in which all the ammonia had been destroyed, was allowed to stand, was shown by the authors to be due to the formation of ammonia from more complex compounds. Egg albumen showed a very marked effect of this kind. The formation of condensation nuclei by the action of light on moist chlorine was also studied, but satisfactory evidence of their production from this action

was not secured. A number of authorities have claimed that a definite proportion of the rays absorbed during chemical change are expended in bringing about the change. If this is true a mixture of air and chlorine should absorb less light than a mixture of hydrogen and chlorine; but the present investigators found the extinction coefficient to be almost the same whether hydrogen and chlorine or oxygen and chlorine were the mixtures used.

Although the cause of the induction period has been discovered, the authors are unable to suggest any explanation of the phenomena without introducing suppositions for which no experimental results have hitherto been presented. J. E. G.

REVIEWS.

THE ELECTRICAL NATURE OF MATTER AND RADIOACTIVITY. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. New York: D. Van Nostrand Co. 1906. pp. viii + 212. Price, $2.00.

The progress of physics during the decade following the discovery of radioactivity has brought forth a great number of significant facts, and a brilliant theory which not only accounts in a reasonably satisfactory manner for these facts, but also bids fair to modify profoundly the fundamental ideas of several sciences besides physics,—certainly chemistry, and very possibly mineralogy, geology and astronomy. There are thus many persons who, while lacking the time for a detailed study of these subjects, feel the need of more accurate knowledge than can be obtained from popular accounts of the wonders of radium.

It is to fill this need that Professor Jones' book is designed; those who, from an acquaintance with his previous books, are familiar with his marked ability in exposition, will not need to be told that this design has been most successfully carried out. The style is simple and non-technical, yet scientific accuracy is seldom sacrificed to simplicity of statement. To give a proper idea of the subject, the author has found it necessary to include many related topics, such as the ionization of gases, the nature of the cathode rays and the Röntgen rays, J. J. Thomson's model atoms, etc.; and, notwithstanding the brevity to which he has restricted himself, he has been able, by skilful arrangement and careful attention to perspective, to give an account of these subjects which is adequate for the purpose in hand.

When one considers the difficulties which the author of such a book has to overcome, it is not surprising that some of his

statements leave room for difference of opinion. Thus, it is probable that few physicists would agree with the implication, on pp. 22 and 23, that the hypothesis of the electrical nature of mass has any connection, even a remote one, with Ostwald's dynamically unsophisticated view that energy is the only reality and matter a mere hypothesis. Again, on p. 58, Runge and Precht's calculation of the atomic weight of radium, 257.8, is defended, as against Mme. Curie's determination, 225, by the argument that, as radium is more active than uranium, we should expect its atomic weight to be greater. Such a simple connection between atomic weight and activity is not suggested by any theory of the structure of the atom, nor is it consistent with the known relations among successive radioactive products. Thus radium emanation is, weight for weight, enormously more active than radium, radium A is more active than the emanation, radium C is less active than radium A, but more active than the emanation, while radium F (polonium) is much less active than even the emanation. If we assumed that the atomic weight followed the activity, we should have here a bewildering series of additions to, and substractions from, the atom which it would be difficult to reconcile with any reasonable view of the process of radioactive change.

The few points, however, upon which the reader may be disposed to differ from the author will play a small part in his final estimate of the book; he can feel only admiration at the very successful solution of what must have been a difficult problem in the exposition of a new and somewhat complicated subject.

H. A. BUMSTEAD.

LES INDUSTRIES DE LA CONSERVATION DES ALIMENTS. By X. ROCQUES. Illustrated. Paris: Imprimerie Gauthier-Villars. 1906. pp. 506. Price, 15 Fr.

This is one of the volumes of the Library of Technology, prepared by M. Rocques, Director of the Laboratory of the General Warehouses of Paris, expert chemist of the Tribunals of the Seine and formerly chief chemist of the Municipal Laboratory of Paris. The introduction was written by M. Brouardel, of the Institute of Technology. The work begins with an historical sketch of the methods of preservation, and gives due credit to the discoveries of Appert, who was really the first to succeed in preserving food by sterilization. This historical sketch although condensed, is highly valuable and presents in small space the most important points in the history of the subject. The four principal methods of food preservation are treated in the following order. The first, sterilization

by heat, extends from p. 64 to p. 231, inclusive. The various technical processes which have been employed are set forth at length, and the directions for the preparing of foods for sterilization are particularly valuable, and are given in detail for all foods of every description. The conservation of foods by cold is the second method treated, from p. 232 to p. 320 inclusive, and modern methods of refrigeration are fully described. The third section is devoted to the conservation of food by desiccation, and extends from p. 321 to p. 427, inclusive. In the methods of drying foods the most modern processes which have been so successfully applied in the case of eggs and milk are not described. These processes were probably not patented in time to be brought to the notice of the author. They consist in injecting the milk or egg in the form of a spray into a large, dry chamber of such a magnitude and kept at such a temperature, that the minute particles of the spray become almost instantly desiccated and fall to the bottom of the chamber in the condition of fine, dry powder. A remarkable point in desiccation of this kind is that the albumen both of the milk and egg, although subjected to a temperature high enough to coagulate it completely under ordinary conditions, remains entirely soluble when dried in this instantaneous manner.

The most important section of the work at the present time is the fourth, devoted to the preservation of food by antiseptics, extending from p. 428 to the end of the work. The author states that in regard to the use of antiseptics for the preservation of food, the greater number of savants and hygienists have expressed themselves as opposed to their employment, while a smaller number favor their toleration in certain minimum quantities. Pasteur is quoted as saying, in 1891, that he advocated a tolerance of them, on condition that the manufacturers make known the nature and quantities of the substances employed. The author sums up the matter by saying that tolerance towards antiseptics has met with only a few partisans among hygienists. The Consulting Committee of Hygiene and the Council of Hygiene have successively condemned the employment of antiseptics. The Congress of Medicine, which was held in 1900, acting on a report made by MM. Brouardel and Pouchet, adopted the following resolution:

"In view of the many injuries pointed out by the authorities in different countries, resulting from the habitual use of foods and drinks preserved with chemical substances, the employment of these substances, namely, borax, salicylic acid,

saccharin and formaldehyde, in food materials, should be prohibited."

The author concludes, from a study of all the literature available, that it seems rational to prohibit, in a general manner, the use of antiseptics in food products, for if a large tolerance in regard to their employment were to be permitted we should absorb daily large quantities of drugs in our food, and this would assuredly be attended, in many cases, with unpleasant and serious consequences.

In regard to sulphurous acid, however, the author remarks that its use has been established by long practice and that it is the only antiseptic whose employment should be regarded as legitimate. It appears, in this respect, that the author has been influenced by the necessities of commerce in his country, and if sulphurous acid is to be permitted for this reason, there is no other antiseptic which will fail to find a like puissant champion, in some country or other.

The author concludes with a description of the different technical methods attending the use of antiseptics, all of which, however, are condemned with the exception of sulphurous acid.

This book will be found useful to all classes of chemists, food inspectors and those engaged in the technical processes pertaining to the preservation of foods. H. W. WILEY.

THE BECQUERREL RAYS AND THE PROPERTIES OF RADIUM. By HON. R. J. STRUTT, F. R. S., Fellow of Trinity College, Cambridge. Second Edition. New York: Longmans, Green & Co. London: Edward Arnold. 1906. pp. 215. Price, $2.40 net.

The appearance of the first edition of this book has already been noted in this JOURNAL.[1] It will, therefore, be sufficient simply to call attention to the fact that a second edition has been called for in such a short time. In the words of the author "This edition has been brought up to date, while some discussions of points doubtful at the time the first edition was published, but now settled, have been omitted."

The comparatively large demand for the book would show that it has met a want. H. C. J.

LEHRBUCH DER ANORGANISCHEN CHEMIE, von PROF. DR. H. ERDMANN, Direktor des Anorganisch-chemischen Instituts der königlichen technischen Hochschule zu Berlin. Vierte Auflage. Mit 303 Abbildungen, 95 Tabellen, einer Rechentafel und farbigen Tafeln. Braunschweig: F. Vieweg und Sohn. 1906. pp. 796. Price, M. 16.

The fourth edition of Erdmann's Inorganic Chemistry shows

[1] THIS JOURNAL, 33, 609 (1905).

thorough revision; it is enlarged from 757 pages to 796; the illustrations are increased from 287 to 303 and a new colored spectrum table—the absorption spectra of the rare earths—is added. Among additions to the text, 3 pages on radium, Van't Hoff's sequence of crystallization of the Stassfurt salts, and Birkeland and Eyde's calcium nitrate process are noticeable and illustrate Erdmann's care to give the latest results of scientific research, and to describe the newest technical processes which have proved, or are likely to prove, commercially profitable.

Erdmann is a chemist of the school which does not favor the introduction of physical chemistry into a text-book of inorganic chemistry. Few modern chemists agree with him. In this edition he has shifted the pages on "Electro-chemie" from the last chapter to a more suitable position in the introductory chapter on general chemistry.

In the review of the second edition of this book by Prof. Richards,[1] the faults of the book—mainly due to Erdmann's attitude toward physical chemistry—are clearly indicated. Yet it must be remembered that "Erdmann," while not too large for study, is the completest, best illustrated, modern, *descriptive* chemistry published, and it should be specially noted that, until the publication last spring of Prof. Alexander Smith's book, all large text-books of inorganic chemistry, giving due attention to physical chemistry, were not only very deficient in descriptive and technical data, but the technical data given were too often obsolete. Hence the deserved popularity of Erdmann's work, as well for study as for ready reference.

E. R.

KURZES REPETITORIUM DER ORGANISCHEN CHEMIE. By DR. KURT DAMMANN. Freiburg im Breisgau: Herdersche Verlagshandlung. 1906. pp. xiv + 256. Price, $1.25.

This little book is based on the author's manuscript notes, which he used for a number of years in the conduct of tutorial classes. The book itself is, of course, not intended to be employed as a text-book, but as a means of rapidly refreshing the memory and, more particularly, for the purpose of quickly preparing for an examination. Works of this class, though extremely plentiful in English, are rather scarce in German. Is the publication of the present one to be regarded as a sign that the examination epidemic, which has raged unchecked for so many years in Great Britain and China, has at last commenced to attack the German Empire? Germany's rivals will sincerely hope so!

[1] THIS JOURNAL, 25, 250.

Dr. Dammann's book is not suited for students who are beginning the study of organic chemistry, but those who have acquired some knowledge of the subject may find it useful for the purposes for which it is intended. The statements in the book are, in general, clear, concise and accurate, and the selection of material appears to have been, on the whole, judicious and careful. J. B. T.

ELEMENTS OF GENERAL CHEMISTRY, WITH EXPERIMENTS. By JOHN H. LONG, M.S., SC.D., Professor of Chemistry and Director of the Chemical Laboratories in the Northwestern University Medical School. Fourth edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1906. Price, $5.00.

In the preface to this edition the author states that "some additions have been made in the presentation of chemical theory and in the description of new substances. Most of the added matter is given in a chapter not in the older editions, on the theories of solution and the conditions of chemical equilibrium."

This book is intended for freshman students of chemistry and is well adapted for the purpose. The author has avoided the very common mistake of introducing too much theory at this stage and has only given enough to make the experiments intelligible. The latter are well selected and clearly set forth; the descriptive part is concise and yet not lacking in important details. While there is no essential difference in the nature of the matter nor in the method of its presentation from other text-books of a similar grade, this book is as satisfactory as most of those in this field and may fill the need in some cases better than others of its kind. J. E. G.

THE CYANIDE PROCESS. An Introduction to the Cyanide Process Including the Determination of the Applicability of the Process to an Ore. By ALFRED S. MILLER, formerly Professor of Mining, Metallurgy and Geology, University of Idaho. Second edition, revised and enlarged. New York: John Wiley & Sons. 1906. pp. 95. 28 Figures. Price, $1.00.

The preface to this manual says: "This book was written primarily for the writer's students in doing laboratory work. The demand from most of the gold mining regions of the world for copies of this book has made it necessary to issue a second edition." "This book has not been written for the expert . . . but for the larger number of persons who have no knowledge of the subject."

The book is abundantly illustrated, the chemistry of the cyanide process and of its modifications is clearly explained, descriptions of the various patented processes are given, but the distinctive and essential value of the work lies in its simplicity

and clearness, enabling mining men with little knowledge of chemistry to understand the details of the process. E. R.

A LABORATORY HANDBOOK FOR THE ANALYSIS OF MILK, BUTTER AND CHEESE. By JAMES RITTENHOUSE EVANS, B.S. New York: Arthur M. Allen. 1906. pp. 60.

This small work of 60 pages contains schedules of the principal examinations of milk by approved methods. No attempt is made to enter into detail, or to explain the principles upon which the processes depend. The manual will be useful to chemists who are not accustomed to milk analysis and who do not wish to take the trouble to look through standard works for the occasional analyses required. In addition to milk analysis, there is a short chapter on the examination of cheese and a longer treatment of butter examination. In the appendices are found certain of the standards of purity for food products contained in circular No. 10 of the Office of the Secretary of Agriculture, but only in so far as these standards pertain to milk, butter fat, cream, butter and cheese. There is also appended a description of the Babcock method of determining fat in milk. H. W. WILEY.